SEPARATION AND IDENTIFICATION OF ISOMERIC HYDROCARBONS BY CAPILLARY GAS CHROMATOGRAPHY AND HYPHENATED SPECTROMETRIC TECHNIQUES

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Abstract

An overview of author's research activities in gas chromatography of isomeric hydrocarbons is presented. The similarities in the properties of isomeric hydrocarbons and the complexities of hydrocarbon mixtures lead to capillary gas chromatography as the most promising method for their individual analysis. The priority of separation systems hyphenating the high efficiency of capillary columns with high isomeric selectivity of liquid crystalline stationary phases for separation of positional and *cis-trans* isomers as well as diastereoisomeric hydrocarbons is demonstrated. The possibility of the separation of positional isomers with functional group in the middle of carbon chain of molecule with new structural trait, which are the most difficult separable positional isomers, is the unique separation characteristic of the liquid crystalline phases in gas chromatography. One of the principal reasons of poorer reproducibility of hydrocarbon retention indices is adsorption of analytes mainly on the interface surface of polar liquid stationary phase with gas phase, e.g. in capillary columns coated with different film thickness of Carbowax 20M the reversed retention order of *cis* and *trans-n-alkenes* was obtained. Because the homology and isomerism, the structure-retention relationships on homologous series are most interesting as the mean of hydrocarbons identification. The most suitable is non-linear asymptotical decreasing dependence of homomorphy factors on the number of carbon atoms of homologous. This fine dependence allowed to discover anomalous retention behaviour of some homologues of different homologues series, the phenomenon was explained and called propyl effect. The unknown boiling points of isomeric hydrocarbons were correlated from the measured retention indices with precision $\pm 0.1^{\circ}C$. The mass and infrared spectra of isomeric hydrocarbons can be quite similar leaving the retention index system as the basic alternative for their identification. However, in other cases, the mass spectra of isomeric hydrocarbons are different and allow the deconvolution of gas chromatographically unseparated isomers.

Keywords: *Isomeric hydrocarbons; GC separation, identification and characterization; GC-MS-FTIR*

1. Introduction

Hydrocarbons represent important industrial raw materials, semiproducts, and products as well as significant pollutants in environment[1]. Therefore analytical chemistry dedicates to development of new methods of their analysis permanent attention. The variety of types and great number of hydrocarbon components is typical characteristic for the crude oil and the fractions of its processing. This is connected with homologism, and particularly with the isomerism of hydrocarbons because the number of possible isomers geometrically increases with increasing number of the carbon atoms in the molecule. For example there are more than 4 billions of possible isomeric alkanes of C_{30}. Because the contemporary gas chromatography has ability to analyze *n*-alkanes approximately up to C_{130}, the number of analyzable hydrocarbons is giant.

The detailed analysis of individual hydrocarbon iso-

mers can be also important, because they show different reactivity, provide products of different quality, or individual isomers can show a different degree of biological activity or toxicity. The increasing requirements to analyse isomeric compounds emphasizes the importance of the study of suitable separation systems and methods of their individual identification. The pretentiousness to solve of these problems is connected with the similarity of physicochemical characteristics of the hydrocarbon isomers. The similarities in the properties of isomeric hydrocarbons and the complexities of hydrocarbon mixtures lead to capillary gas chromatography as the most promising method for their total analysis.

This paper provides an overview of author's and co-workers activities on the petrochemical and academic research in the use of capillary gas chromatography for the characterization and analysis of hydrocarbons [2,3].

2. Model mixtures

The lack of standard reference hydrocarbon materials was overcome by using characteristic reaction products prepared mainly by methylene insertion reaction, isomerization and catalytical dehydrogenation [4]. The obtained products were separated by preparative displacement liquid chromatography on silica gel by fluorescence indica tor adsorption method (FIA) according to hydrocarbon types. Thus the model mixtures of isomers or congeners of particular hydrocarbon types as alkanes, alkenes, alkadienes, alkynes, cycloalkanes, cycloalkenes, cycloalkadienes and aromatic hydrocarbons were obtained. Such mixtures completed by some available standard reference materials of hydrocarbons were used for the study of their separation and identification by means of capillary gas chromatography.

3. Separation

The basis assumption of gas chromatographic analysis is separation of analyte from other compounds of analysed mixture. The high efficiency and isomeric selectivity of gas chromatographic capillary columns were investigated for the separation of isomeric hydrocarbons with similar physicochemical properties. The extremely high efficient separation systems were prepared by using of long capillary columns (up to 300 meters), small inner diameter (up to 100 µm), thin stationary phase film (up to 0.01 µm), and by recycling of analyte in the capillary column.

The extremely efficient capillary column (up to 700 000 effective plates) with dimensions 200 m x 0.25 mm coated with nonpolar stationary phase Apolan was prepared [5]. This efficiency is close to the highest efficiency obtained in gas chromatography also in columns with small inner diameter [6]. Such column efficiencies were used to study the separation of all positional and *cis-trans* isomeric C_{15}-C_{19} *n*-alkenes [7-9].

3.1. Positional isomers

It is evident from chromatograms of *n*-octadecene isomers (Fig. 1 a) that the separation of neighbouring positional isomers had been gradually getting more difficult with the shift of the double bond from the end to the middle of the carbon chain of the molecule. The positional isomers *cis-* as well as *trans-* with double bond in the middle of the molecule carbon chain, in this case the isomers with new structural trait, i.e. *cis-9-,* resp. *trans-9-*octadecene, are not separated even in such extremely efficient column. The efficiencies up to about 10 millions plates were calculated for the quantitative separation of the positional isomers with functional group in the middle of the carbon chain of the molecule with the new structural trait [7].

The similar separation of positional isomers was achieved also by using extremely efficient capillary column with polar stationary phase Carbowax 20M (500 000 plates) (Fig. 1 b) [7]. This result was explained with the fact that for separation the positive effect of the increasing shielding of polar interactions when double bond is shifted

from the end to the middle of the carbon chain of the molecule is eliminated by the adsorption of positional isomers on the interface surface polar stationary phase - gas phase increasing in the same direction. The polarity of positional isomers of *n*-alkenes decreases with the shift of the double bond from the end to the middle of the carbon chain and in this direction increases the adsorption of isomers.
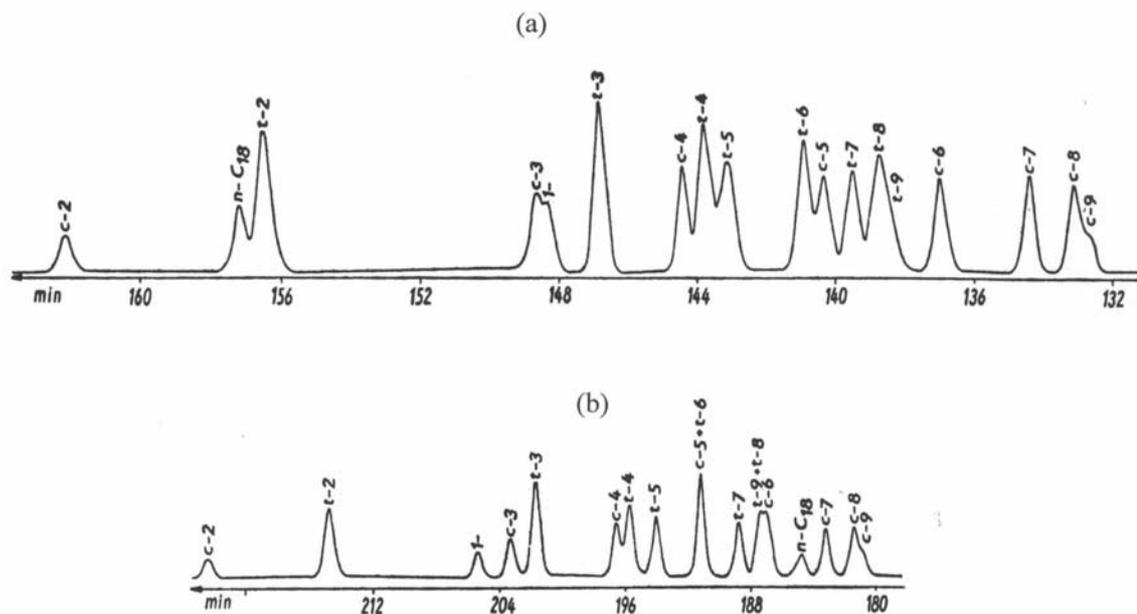

Fig. 1. Chromatograms of the separation of *n*-octadecene isomers in: (a) 200 m column with Apolan at 160 °C and 0.3 MPa H$_2$; (b) 300 m column with Carbowax 20M at 110 °C and 0.3 MPa N$_2$.
t - *trans*, c - *cis, n*-C$_{18}$ - *n*-octadecene.

These results oriented further study of isomeric hydrocarbons separation to the separation systems combining high efficiency of capillary column with isomeric selectivity of stationary phases. The isomeric selectivity of stationary phases was characterized by the selectivity factors α for *para-/meta-xylene* [8] . The α-values for different stationary phases are compared in Table 1. It is evident that on the common polar (Carbowax 20M, OV-22) or nonpolar (Squalane, OV- 1) stationary phases the *α*-values are close to 1. The lowest and the highest α-values are shown by stationary phases α-cyclodextrine, resp. rubidiumbenzenesulphonate, which, however, do not allow the preparation of high efficient capillary columns. Some liquid crystals as stationary phases show relatively high *α*-values, e.g. 4-methoxy-4'-ethoxyazoxybenzene (MEAB) α =1.14 at 80°C and permit also to prepare the high efficient capillary columns. Considering the investigated liquid crystals, the highest α-value = 1.21 was measured at 65°C on liquid crystalline polymer stationary phase (4-octyloxy(4-alkyloxyphenyl benzoate)) polymethylhydrogen siloxane (POBAP-20) with optimized film thickness [10] .

The significance of the selectivity contribution of liquid crystalline stationary phase to the isomers separation is documented comparing of the separation of all isomeric *n*-dodecenes on a 300 m column coated with Carbowax 20M as stationary phase with an efficiency of 500 000 plates and on 90 m column with MEAB liquid crystalline stationary phase having a efficiency of 200 000 plates [8] . It is evident that in the MEAB column all *trans-* and *cis*-positional isomers including isomers with double bond in

the middle of the carbon chain with new structural trait *(cis-6-,* resp. *trans*-6-dodecene) are separated in substantially shorter time of analysis (Fig. 2). Moreover, in the case of isomers *trans-5/trans-6-dodecenes* even the elution order of positional isomers was changed.

Table 1

Selectivity factors *α* for *para-/meta*-xylene on different stationary phases

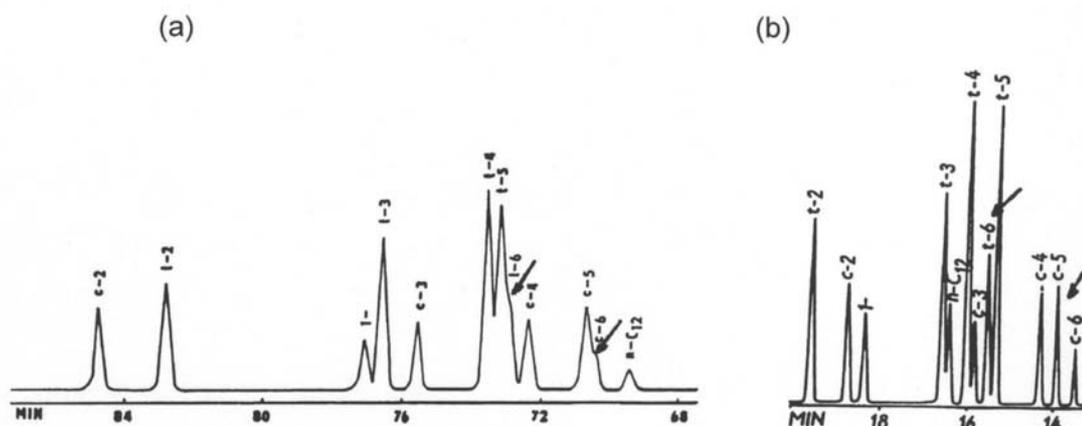| Stationary phase	Temperature (°C)	Selectivity factor *α* (*para-/meta*-xylene)
Rubidiumbenzensulphonate	80	0.79
Carbowax 20M	80	0.96
Squalane	80	0.98
Silicone OV-22	80	0.99
Silicone OV-101	80	1.01
A-DEX 120	70	1.09
4-Methoxy-4'-ethoxyazoxybenzene	80	1.14
POBAP-20	65	1.21
α-Cyclodextrin	100	3.80

Fig. 2. Chromatograms of the separation of *n*-dodecene isomers in: (a) 300 m column with Carbowax 20M at 43 °C and 0.3 MPa H_2; (b) 90 m column with MEAB at 90 °C, ū =35 cm.s^{-1} H_2.

This interesting retention behaviour of positional isomers on liquid crystalline phase was explained on the basis of the dependence of *α*-values on the number of the carbon atoms in molecule for all neighbouring positional isomers of C_{11}-C_{13} *n*-alkenes on the liquid crystalline (OBO) and squalane stationary phases, respectively [11,12] (Fig. 3). The *α*-values are higher on the liquid crystalline phase, it means that the selectivity for positional isomers increases with the shift of the double bond from the middle to the end of the carbon chain of molecule. Because the positional

isomers also eluate in the same direction the conditions for their separation on mesogenic phase are easier than on the nonmesogenic phases. The exceptional is *α*-value for the pair *trans-5-/trans-6-dodecenes* when isomer with position of functional group more to the centre of molecular chain exhibits higher retention as an isomer with functional group more to the end of molecular chain. This result is connected with the effect of alternation of retention of *n*-alkene homologues and positional isomers on the liquid crystalline phase (Fig. 3 and 4). The retention of *trans*-isomers with an even position of the double bond and *cis*-isomers *n*-dodecenes with an odd position of the double bond is increased, because their molecular chain is more oriented in the direction of the molecular axis of isomers. It causes more drawn-out shape of molecule and therefore also increasing of retention on the liquid crystalline phase. It reflects in reversed retention order of *trans-5-* and *trans-6-dodecenes* and in increase of the retention difference of *cis-5-* and *cis-6-dodecenes*. The possibility of the separation of positional isomers with functional group in the middle of the carbon chain of molecule with new structural trait, which are the most difficult separable positional isomers on the nonmesogenic phases, is the unique separation characteristic of the liquid crystalline stationary phases in capillary gas chromatography.
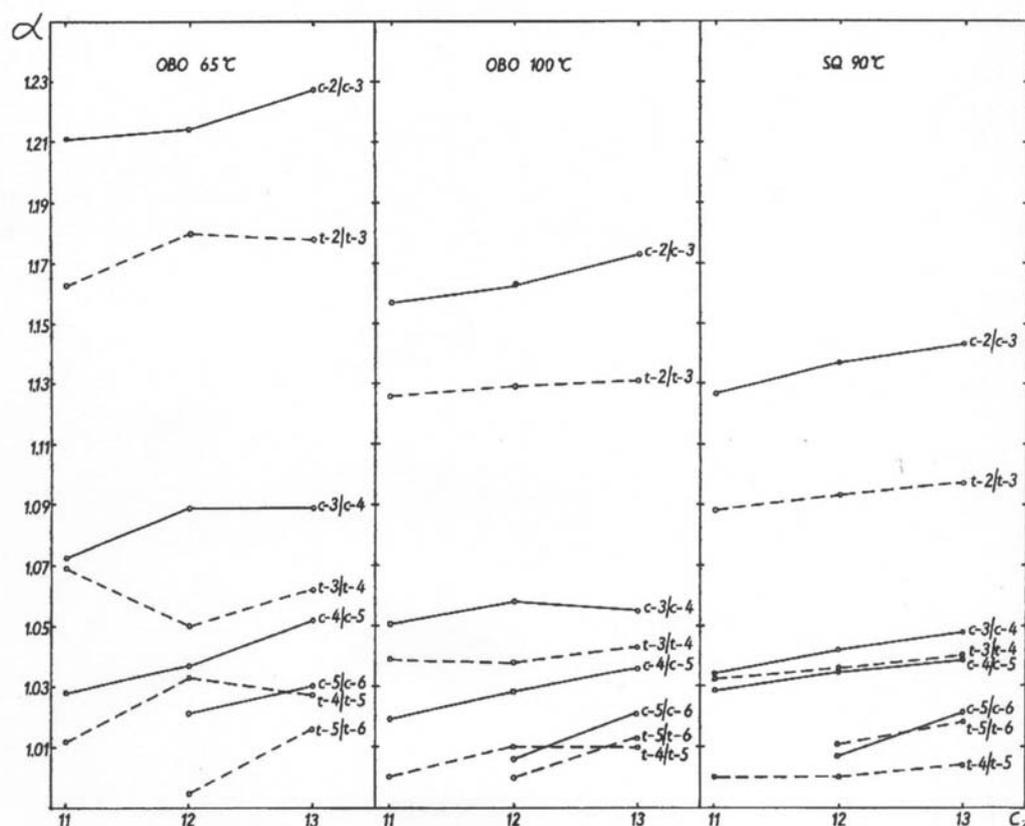

Fig. 3. Dependence of selectivity factors of C_{11}-C_{13} positional *n*-alkene isomers on number of carbon atoms for liquid crystal OBO and squalane as stationary phases.
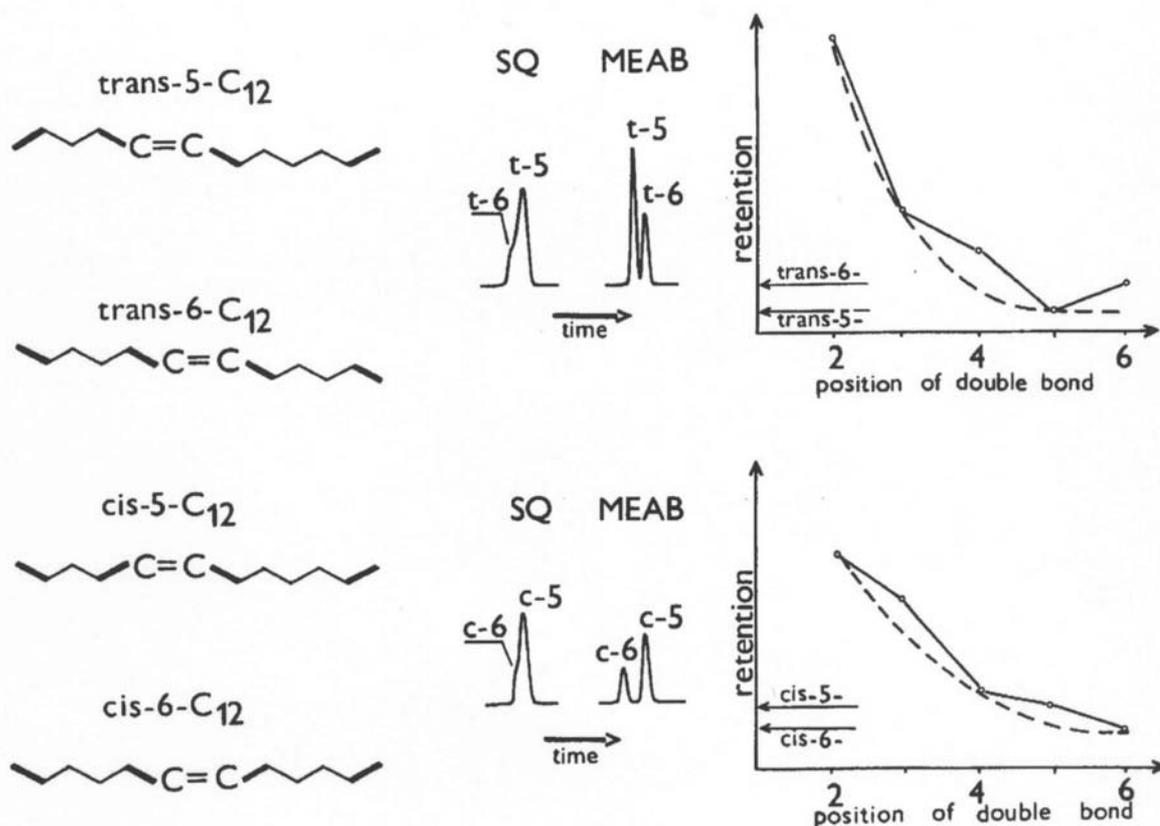
Fig. 4. Changes in retention of isomeric *trans* and *cis* dodecenes with change of the position of double bond on a liquid crystal MAEB as stationary phase.

The alternation effect of retention was observed on liquid crystalline phases for all types of hydrocarbons studied. For example in *n*-alkynes, 1-alkynes with an odd number of carbon atoms, 3-alkynes with an odd number of carbon atoms, etc. exhibit an increased retention [13]. In alkylbenzenes, the *n*-alkylbenzenes with an odd number of carbon atoms in the molecule and those dialkylbenzenes having an odd number of carbon atoms in the main (longer) chain exhibit an increased retention [14].

3.2. Cis-trans isomers

On nonpolar squalane phase obtained retention data allow the characterization of *cis-trans n*-alkenes retention. In Fig. 5 the retention behaviour of corresponding pairs of C_6-C_{13} *cis*- and *trans-n*-alkenes with double bond in posi-tion 2- to 6- on squalane at 100 °C is presented. It is evident that the statement that *trans*-isomer elutes before the corresponding *cis*-isomer is valid only for alkenes up to C_9. In isomeric 2-alkenes, the *trans*-isomers are eluted first. However, the 3-isomers change the retention sequence gradually when the carbons atom number in the molecule is increased, with lower alkenes *trans*-3-alkenes, and with higher alkenes the *cis-3* -alkenes, are eluted first. The change in the retention sequence of the 4-isomers gradually increases faster than that of 3-isomers. With more internal isomers e.g. double bond in positions *5-,* 6- and 7-, the *cis*-isomer is eluted first.
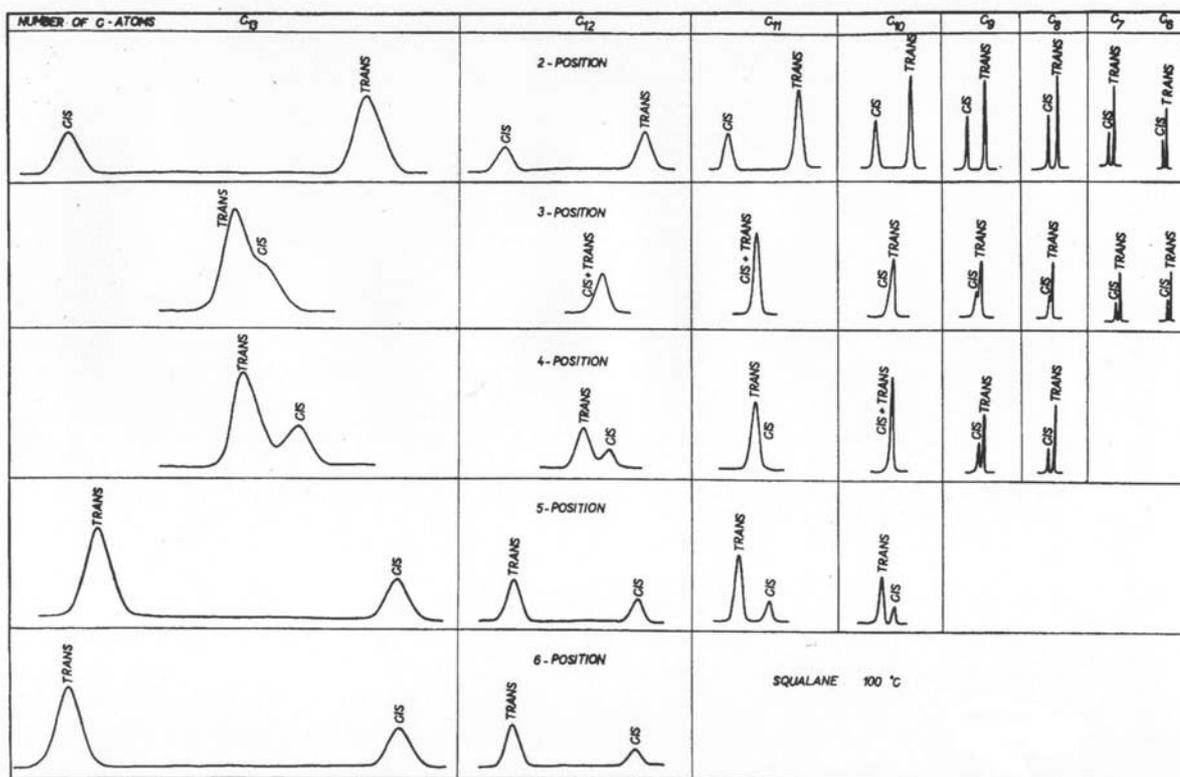
Fig. 5. Separation of *cis/trans-* corresponding C_6-C_{13} *n*-alkene isomers as a function of the position of double bond and the number of carbon atoms on squalane at 100 °C.

Since the retention order of corresponding *cis-* and *trans-* alkene isomers on nonmesogenic phases is generally different [15-17] their separation on mesogenic phase can be better or worse than on nonmesogenic phase. Separating *cis-/trans-* alkene isomers the selectivity of the liquid crystalline phase is higher for *trans-* as for corresponding *cis-*isomers, in accordance with more stretched shape of their molecules [11]. On the liquid crystalline MEAB phase all *trans-n*-dodecenes have higher retention than the corresponding *cis-*alkenes. From the comparison of retention indices differences Δ(δI) of *cis-*trans *n*-dodecenes isomers on MEAB and squalane Δ(δI) in Table 2 the increased retention of *trans-n*-dodecene isomers with an even position of the double bond and also the effect of isomers retention alternation is obvious [8]. For the optimization of the separation of *cis-/trans-*isomers on liquid crystalline phase their different temperature dependence of retention can be used. On all studied stationary phases the temperature coefficients of retention for straight as well as branched alkene *cis-*isomers are higher than for the corresponding *trans-*isomers. On MEAB the differences of *dI/dT cis-*isomers - *trans-*isomers ≈ 0.2 i.u./°C, are substantially higher as on nonpolar phase squalane ≈ 0.03 i.u./°C.

Table 2

Differences in retention indices δI of *cis-trans* isomers of *n*-dodecenes on MEAB and squalane at 87 °C

Cis-trans isomers	δI		$\Delta(\delta I)$
	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

3.3. Diastereoisomers

From comparison of the retentions of most difficult separable C_8-C_{10} diastereomerie alkanes on mesogenic and nonmesogenic phases in Table 3 it is evident that liquid crystalline phases (PBO, PBHP) can be more advantageous than nonmesogenic phases also in the separation of the hydrocarbon diastereoisomers [18]. The problem of separation of relatively lower-boiling diastereoisomers 3,4-dimethylhexane with low retention factor on mesogenic phase was solved by using a column with smaller inner diameter (decreasing the phase ratio β) 112 m x 110 μm (Fig. 6) [19]. Generally, the better separation of diastereoisomers on a liquid crystalline phase could be obtained if the isomer with the more elongated molecular structure has nearly the same retention as the other on a non-mesogenic stationary phase.

Table 3

Difference in retention indices δI for diastereomeric C_8-C_{10} alkanes on the different stationary phases at 40°C

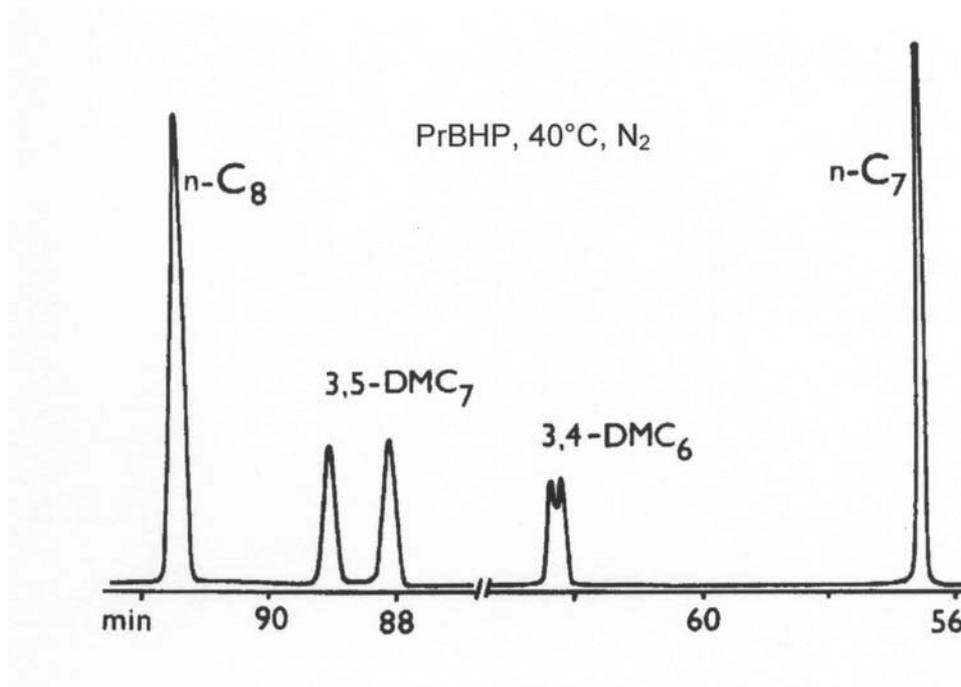| *Diastereomeric* alkane	*Squalane*	*Ucon LB*	δI *SE-30*	*PBO*	*PrBHP*
3,4-Dimethylhexane	0.0	0.0	0.3	0.0	0.9
3,5-Dimethylheptane	0.0	0.0	1.1	1.5	3.3
3,6-Dimethyloctane	0.0	0.0	0.8	1.1	2.4

Fig. 6. Separation of diastereoisomeric 3,4-dimethylhexane and 3,5-dimethylheptane in column 112 m x 0.11 mm coated with liquid crystal PrBHP, 40°C.

3.4. Enantiomers

The combination of a very high column efficiency in recycle capillary gas chromatography and at least low chiral selectivity of stationary phase has been suggested to solve the problem of difficult separable enantiomers, resp. stereoisomers [20]. The new arrangement of recycle capillary gas chromatography has been proposed replacing the recycle valve by a peristaltic pump. Possibilities of this systems have been demonstrated on the separation of 3,4-dimethylhexane stereoisomers. This hydrocarbon consist of a pair of diastereoisomers (1:1), where one diastereoisomer is a racemic mixture of enantiomers and the other one is an achiral mesoform. Their gas chromatographic separation on an achiral stationary phase and a chiral stationary phase give two peaks with a quantitative ratio 1:1 and three peaks with 1:1:2 ratio, respectively (Fig. 7). The selectivity factor for 3,4-dimethylhexane diastereoisomers on OV-1 at 30 °C $\alpha = 1.006$, for comparison on liquid crystalline phase 4-n-pentyl-benzoic acid 4',5-n-hexylpyrimidine-2-ylphenyl ester (PBHP) $\alpha = 1.049$. The selectivity factor for 3,4-dimethylhexane enantiomers on Chirasil-β-Dex (30% w,w in OV-1701) at 50 °C is $\alpha = 1.08$ and for the second enantiomer and meso form $\alpha = 1.009$. The applied efficiencies of recycle capillary GC were up to 2 million plates.
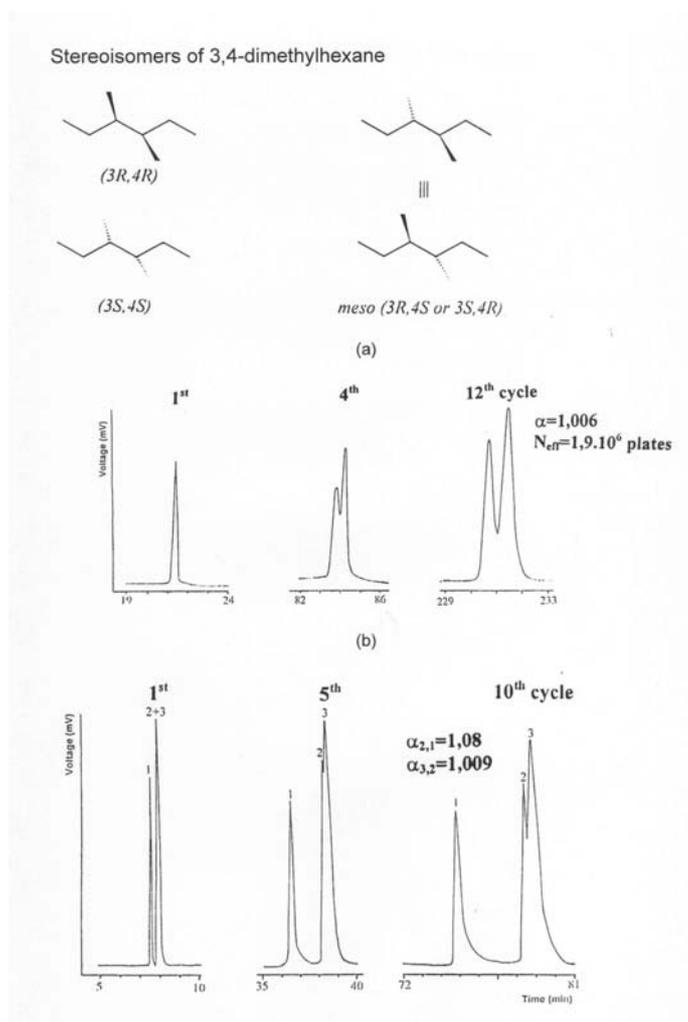
Stereoisomers of 3,4-dimethylhexane

(3R,4R)

(3S,4S)

III

meso (3R,4S or 3S,4R)

(a)

1ˢᵗ   4ᵗʰ   12ᵗʰ cycle

$\alpha=1,006$
$N_{eff}=1,9.10^6$ plates

(b)

1ˢᵗ   5ᵗʰ   10ᵗʰ cycle
2+3   3

$\alpha_{2,1}=1,08$
$\alpha_{3,2}=1,009$

Fig. 7. Separation of stereoisomers 3,4-dimethylhexane in: (a) 50 m x 0.32 mm x 0.2 μm OV-1, 30 °C; (b) 50 m x 0.25 mm x 0.2 μm Chirasil-β-DEX, 30 % selector, 50 °C; 1,2-enantiomers, *3-meso* form.

3.5. *Complex mixtures*

The priority of separation systems hyphenating the high efficiency of capillary columns with high isomeric selectivity of liquid crystalline stationary phases for the separation of complex mixture of congeners is documented on the separation of the process OLEX products (all isomeric C_{10}-C_{13} *n*-alkenes and *n*-alkanes) in comparison with the separation on column of similar efficiency coated with nonmesogenic siloxane stationary phase (Fig. 8)[8]. In agreement with previous discussion, the retention range of isomeric *n*-alkenes on liquid crystalline phases, defined as the difference between the highest and the lowest retention index of isomers, is substantially greater (Table 4). It creates the better conditions for separation of complex mixture of C_{10}-C_{13} *n*-alkene congeners in comparison to nonmesogenic stationary phases.
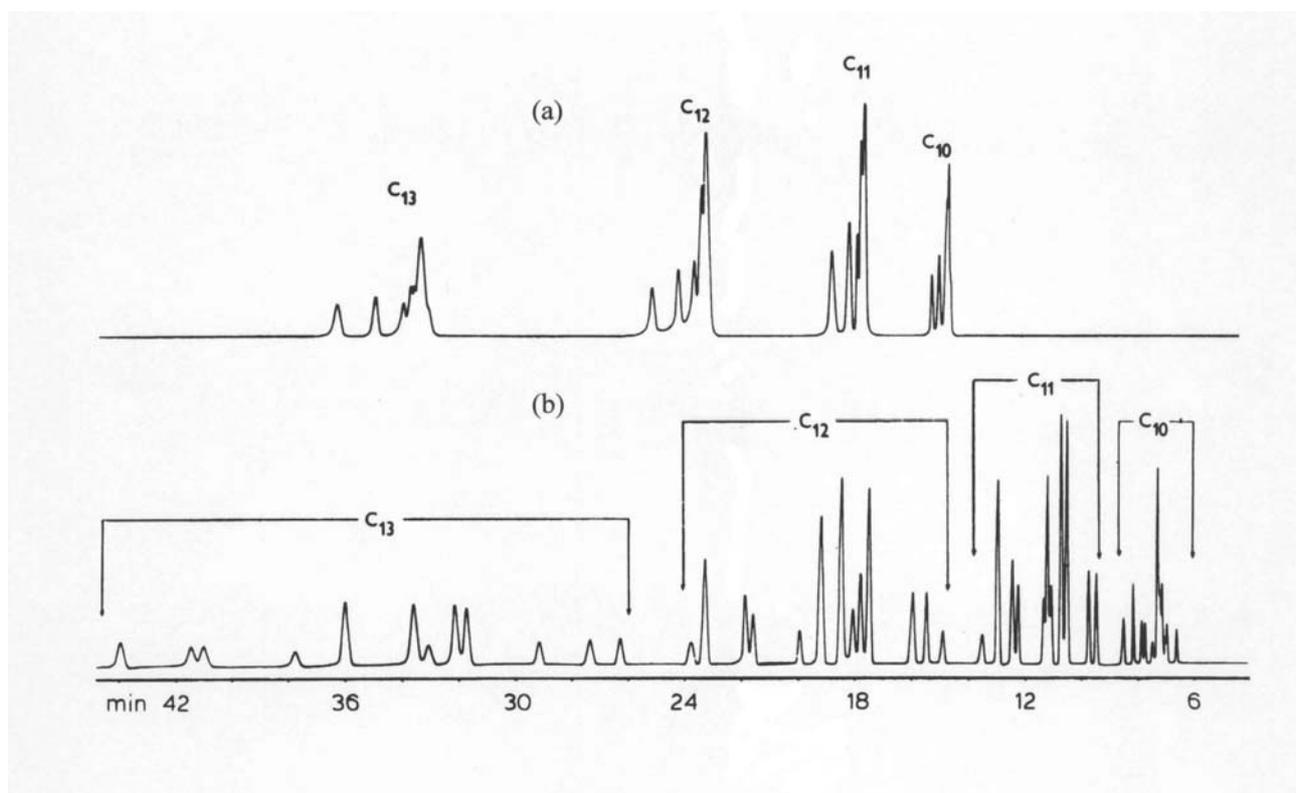
Fig. 8. Separation of OLEX product, C_{10}-C_{13} *n*-alkenes and *n*-alkanes, obtained in: (a) 100 m x 0.25 mm column coated with silicone oil DC-550, 110 °C; (b) 90 m x 0.25 mm column with MEAB at 80 °C.

Table 4

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	983.0 – 1005.7	22.7
7,8-Benzoquinoline	998.0 – 1028.0	30.0
Di-n-butyl tetrachlorophthalate	998.0 - 1029.8	31.8
Polyethylene glycol 4000	1035.7 – 1068.9	33.2
4-Methoxy-4'-ethoxyazoxybenzene at 70 °C	973.3 – 1030.0	56.7

The obtained results demonstrate the importance of liquid crystalline stationary phases in capillary gas chromatography for separation of all types of isomeric hydrocarbons. In the case of multicomponent mixtures of different hydrocarbon types, the separation of analysed mixtures in high efficient capillary column with nonpolar stationary phase followed by cryofocusing and injection of nonseparated peaks in to the second capillary column coated with isomeric selective (and middle polar) liquid crystalline i.e. phase by using multidimensional capillary GC [21] can be the most efficient tool for their separation.

4. Identification

The identification of isomeric hydrocarbons is usually a most difficult stage of gas chromatographic analysis. The problems in identification of gas chromatographic separated hydrocarbons are connected with the lack of reference materials, the lack of published retention data as well as their insufficient reproducibility, further more with insufficient precision of the structure-retention relationships, resp. retention calculation methods, and with the limitations of hyphenated chromatographic-spectrometric techniques (GC-MSD-FTIRD) as the means for the isomeric hydrocarbons identification as well.

4.1 Retention data

The logarithmic retention index (Kováts retention index), *I,* is recommended for the identification of analytes on the base of retention data [22]. In gas chromatography it is possible to achieve high precision of retention indices measurement, which is characterized by standard deviation about 0.01 i.u. However, the interlaboratory reproducibility of retention indices is substantially lower. For example in Sadtler's library [23] of retention indices obtained under standard conditions, the reproducibility of retention indices of analytes measured on the polar stationary phase Carbowax 20M not better than 2 i.u. is declared. By our opinion, this result can also be explained with differences in inner diameter of capillaries and corresponding differences in prepared film thickness of liquid stationary phase due to assertion of the solute interface adsorption.

4.1.1 Interface adsorption

One of the reasons of poorer reproducibility of hydrocarbon retention indices is the fact that in the gas-liquid chromatography besides absorption also adsorption of analytes on the interface surface of stationary liquid phase with carrier gas and inner wall of capillary colunm is acting [24]. In this case the relative retention data in form of relative retentions, r_{is}, and retention indices, are dependent on the amount of stationary phase in the column and the properties of the inner wall of column. For separation systems in which the hydrocarbons are analyzed on polar stationary phases the adsorption interactions of the analytes at the polar liquid phase - gas phase interface are characteristic.

In Table 5 the values of relative retention of alkylbenzenes are given, measured on two capillary columns with different film thickness of Carbowax 20M [2]. By diminishing the film thickness of stationary phase the relative retention of alkylbenzene pairs may increase or decrease. At thinner film phase the relative contribution of adsorption on surface interface polar stationary phase - gas phase to analyte retention is larger and this effect is inverse proportional to polarity of an alkylbenzene. Therefore, when an alkylbenzene congener with higher carbon atoms (less polar congener) has a higher retention than a reference alkylbenzene on column with thicker film stationary phase, on column with thinner film the relative retention is higher, and vice versa. In the case of alkylbenzene isomers with decreasing of film liquid thickness, the relative retention is similar but not equal because of different isomers polarity.

Table 5

The values of relative retention r_{is} of C_{15}-C_{16} alkylbenzenes in two Carbowax 20M capillary columns with different film thickness of Carbowax 20M as stationary phases ($d_f^{CW-1} < d_f^{CW-2}$)

Pair of alkylbenzenes	Number of C atoms	r_{is}^{CW-1}		r_{is}^{CW-2}
1-ethyl-2-heptyl-/1-propyl-2-hexylbenzene	C_{15}/C_{15}	1.225	≈	1.227
1-pentyl-2-pentyl/*n*-nonylbenzen	C_{16}/C_{15}	1.043	>	1.022
1-methyl-2-octyl/1-pentyl-2-pentylbenzen	C_{15}/C_{16}	1.015	<	1.037
1-propyl-2-heptyl-/1-butyl-2-hexylbenzen	C_{16}/C_{16}	1.055	≈	1.056

The effect of different adsorption of hydrocarbon isomers on the surface interface polar stationary phase - gas phase is documented on Fig. 9 [7, 25]. The mixture of *n*-pentadecene isomers was separated under the same experimental conditions in two capillary columns coated with different film thickness of Carbowax 20M. The values of the retention factor *k* characterizing the film thickness of the stationary phase are 2.1 for *cis*-5-pentadecene in col-

umn A and 1.3 in column B. It can be seen that the retention order of *trans-6*- and *cis-5*-pentadecenes on these columns is reversed. This result can be explained by relative higher contribution of *trans*-isomer adsorption to the retention in column with thinner film stationary phase, because *trans*-isomer is less polar in comparison to *cis*-isomer.
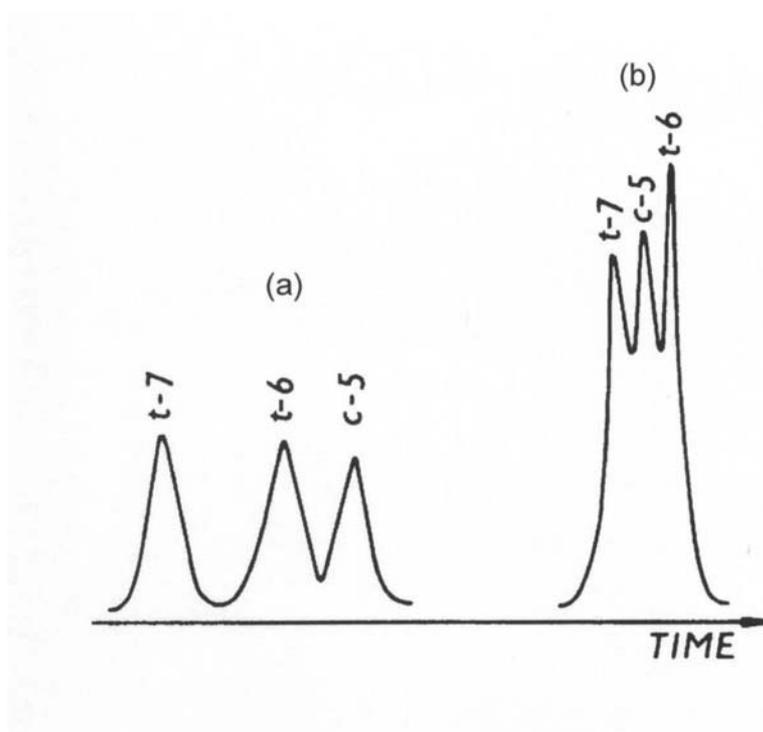

Fig. 9.   Separation of *trans*-7-(t-7), *trans*-6-(t-6), *cis*-5-pentadecene (c-5) at 95 °C and 0.3 MPa H$_2$ in two capillary columns (300 m x 0.25 mm) coated with different film thickness of Carbowax 20M, the retention factors for 1-pentadecene in these columns are 1.36 and 2.25, respectively.

Similarly, the value of hydrocarbon retention index with decreasing film thickness of stationary phase can increase or decrease. Fig. 10 shows the dependence of the retention indices of *o*-xylene and 1-nonyne on the film thickness of apolar squalane phase at 70°C in eight glass capillary columns using capillaries with the wall surface roughened by etching with gasesous hydrogen chlorid and

deactivated by silanization in the gaseous phase with hexamethyldisilazane-trimethylchlorsilane (5:1) before coating [13]. It can be seen that on such columns the retention indices of both these analytes increase as the phase film thickness decreases. Higher retention indices of analytes measured on columns with thinner film of stationary phase result from relatively higher contribution of adsorp-

tion to the retention of polarer hydrocarbon analytes (*o*-xylene, 1-nonyne) on interface liquid phase-wall of capillary column in comparison with *n*-alkanes as reference standards in the retention index system. In the columns with

a squalane film thicker than 0.2 μm the retention indices of *o*-xylene and 1-nonyne are virtually independent on the phase film thickness.
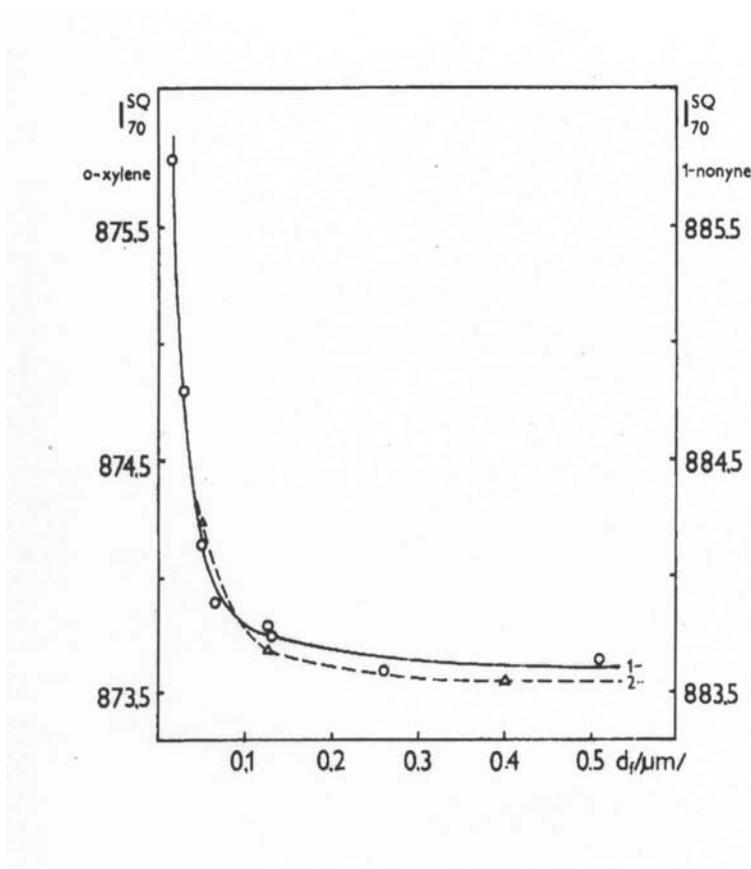

Fig. 10. Dependence of the retention indices of *o*-xylene (1) and 1-nonyne (2) at 70 °C on the film thickness of squalane for eight glass capillary columns roughened with gaseous hydrogen chloride.

On Fig. 11 the dependence of the retention index of *o*-xylene on the retention factor *k* is given obtained by measurement in ten metal capillary columns with different film thickness of 1,2,3-tris-cyanoethoxypropane (TCEP) as polar stationary phase [26]. In this case the retention index of *o*-xylene decreases as the film thickness decreases. Lower retention index of *o*-xylene measured for columns with thinner film phase results from relatively higher contribution of adsorption to the retention of *n*-alkanes as comparing standards on surface interface polar stationary phase - gas phase. This assumption confirms result that by the change of *n*-alkanes for *n*-alkylbenzenes as reference

standards the previous obtained dependence is practically eliminated. Not complete elimination of this dependence is in connection with different polarities of *o*-xylene and *n*-alkylbenzenes; corresponding *n*-alkylbenzenes are less polar and therefore relative more adsorbed in column with thinner polar phase film. From Fig. 11 can be seen that the difference of retention indices of *o*-xylene measured in columns with thinnest and thickest film of TCEP is about 200 i.u., representing approximately one thirds of full Rohrschneider-McReynolds polarity scale for aromatic hydrocarbons.
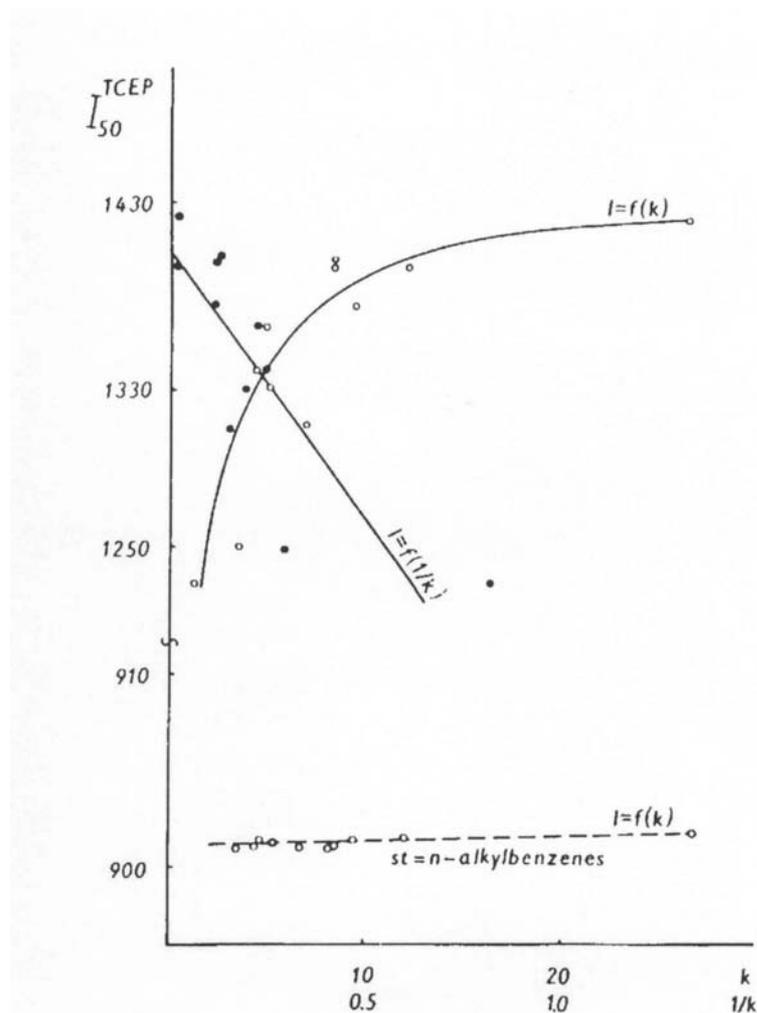
Fig. 11. Dependence of the retention index of *o*-xylene (*n*-alkanes or *n*-alkylbenzenes as reference standards) on retention factor or its reciprocal *(1/k),* obtained by measurement at 50 °C in ten metal capillary columns coated with TCEP.

The stationary phase film thickness in column can be changed in connection with evaporation of the stationary phase from the column during its using. Because the stationary phase evaporates preferentially from the beginning of column, the ratio of absorption and adsorption contributions to the retention of analytes is changed and also their retention index as a consequence [27]. Due to this fact the dependences $I = f(d_f)$ of retention index of benzene on film thickness of TCEP for fresh columns and for the condi-

tioned column are different (Fig. 12). At values $k < 2$, by conditioning column due to evaporation of stationary phase from the beginning of the column also the absolute contribution of adsorption to retention is changed. In this case the retention equation derived for absorption-adsorption mechanism of retention is not valid, because the absolute adsorption contribution to the retention of analyte is changed with the change of film thickness of stationary phase.
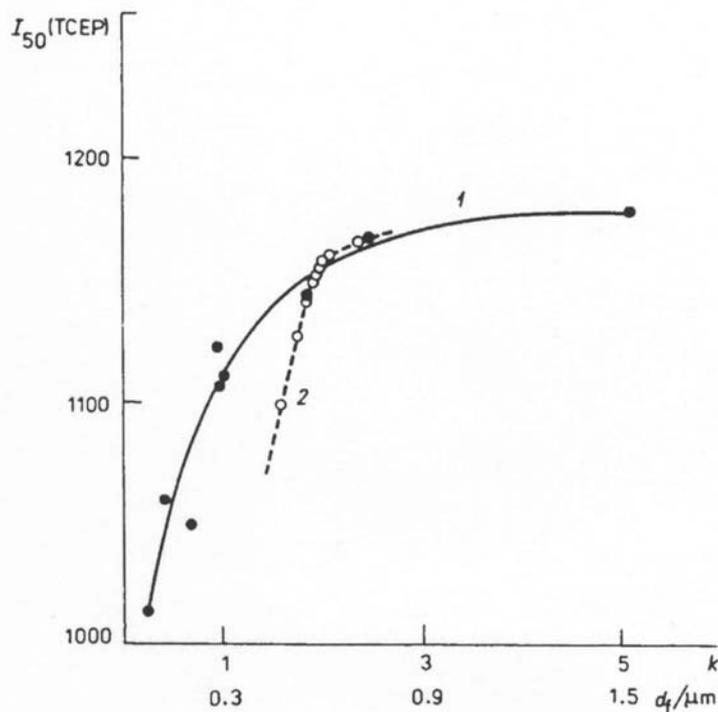
Fig. 12. Change of the retention index in dependence on the film thickness of stationary phase and on the retention factor for benzene in TCEP columns at 50 °C. 1. Dependence I = f(k) for ten fresh prepared columns with different film thickness of stationary phase. 2. Dependence I = f(k) for one column during its conditioning (550 h at 140 °C and 0.2 MPa N_2).

These results underline the problem of reproducibility of retention data and their use for identification. The reproducible retention indices of hydrocarbons can be obtained by using separation systems in which the contribution of interface adsorption plays a negligib1e role [24, 28]. In the analysis of hydrocarbons this condition is better fulfilled by separation systems with a stable nonpolar stationary phases in a column with the lowest possible adsorption activity of the inner walls of the capillary columns.

4.1.2. Temperature coefficient of retention index

Temperature increments of the retention index, the values *dI/dT,* obtained by precise measurement of retention indices at different temperatures, characteristically reflect structural differences not only between classes of hydrocarbons, but also small structure differences of isomeric hydrocarbons and can be used for the confirmation of identification. For example *dI/dT* values of 47 C_7-C_{15} alkylbenzenes and benzene on squalane are in relative broad range 0.02 - 0.45 i.u/°C (Fig. 13) [29, 30]. The largest dI/dT values were observed for alkylbenzenes that have alkyl groups in the vicinal (asymmetric) position (pentamethylbenzene), and the symmetrical alkylbenzene (1,3,5-triisopropylbenzene) have the lowest *dI/dT* values. In case of 1,3,5-triisopropylbenzene the *dI/dT* value is similar to that of *n*-alkane. By introducing of CH_2 group to a dialkylbenzene in *meta*-position the *dI/dT* values decrease and by similar substitution in *ortho*-position the *dI/dT* values increase:

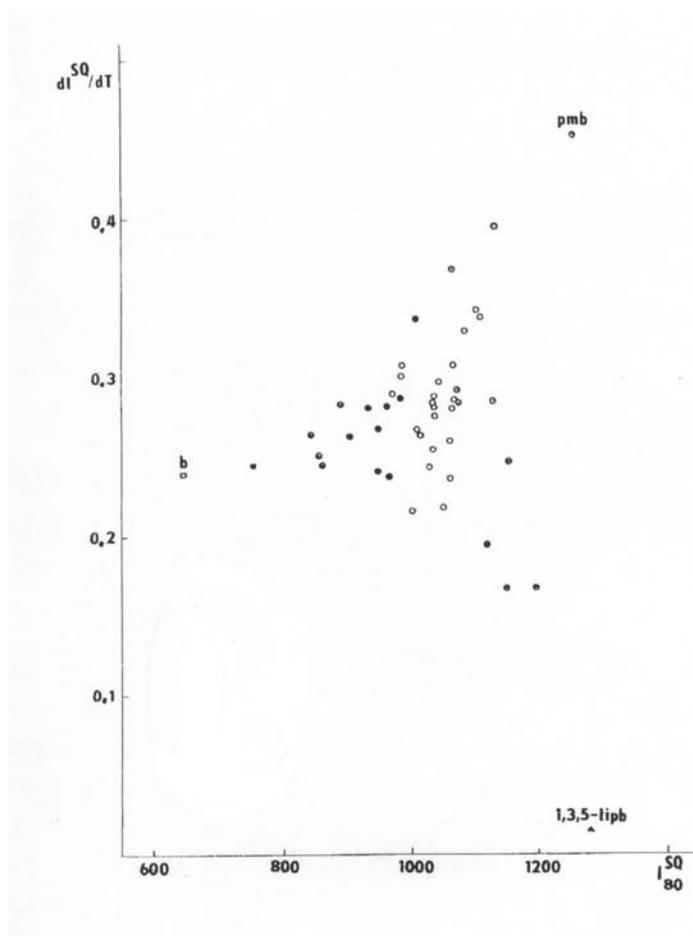|			$\delta(dI^S/dT)$
1-methyl-3-*tert*-butylbenzene	subst.	1,3-dimethyl-5-*tert*-butylbenzene	-0.07
1-methyl-3-ethylbenzene	CH_2	1,2-dimethyl-3-ethylbenzene	0.09

Fig. 13.   Values dI/dT of 47 alkylbenzenes up to C_{15} on squalane as a function of retention index on squalane at 80 °C; b - benzene, pmb - pentamethylbenzene, 1,3,5-tipb - 1,3,5-triisopropylbenzene.

In straight chain as well as branched alkenes, the *cis*-isomers have larger *dI/dT* values than the corresponding symmetric *trans*-isomers [15,16] . This result is significant also with the fact that *cis-/trans*-isomers are difficult, or even impossible to distinguish on the basis of their mass spectra.

4.1.3. Pressure coefficient of retention index

The value of retention indices of hydrocarbons can significantly depend also on the characteristics of carrier gas [31]. The influence of the type and pressure of the carrier gas on the retention indices of hydrocarbons on apolar stationary phase squalane was investigated [13, 29, 30]. As can be seen from Table 6, when hydrogen was replaced by nitrogen as the carrier gas, the retention indices of *o*-xylene and benzene were on 0.45 i.u., those of cyclohexane 0.3 i.u. and those of *n*-alkynes 0.1 i.u. higher for a carrier gas inlet pressure of 0.4 MPa. When the inlet pres-

sure of hydrogen increased from 0.26 to 0.40 MPa the retention indices of *o*-xylene and cyclohexane increased by 0.1 i.u., whereas those of *n*-alkynes were not changed. The changes in the retention indices of isomeric *n*-alkynes on apolar squalane stationary phase caused by a change in the carrier gas and a change in its pressure (0.4 MPa) are within the precision range of measurement. From results in Table 7 can also be concluded that an increase in the inlet pressure and/or replacement of hydrogen by nitrogen as the carrier gas improves the selectivity of the separation of alkylbenzenes vs. alkanes. The magnitude of this effect increases with increasing polarity of the stationary phase from squalane to the TCEP. The increase in the retention index of alkylbenzenes on TCEP up to 3 i.u. was observed when hydrogen (inlet pressure 0.1 MPa) was replaced by nitrogen (inlet pressure 0.2 MPa) as the carrier gas. The pressure coefficients of the retention index, *dI/dP* values [32], of alkylbenzenes indicate fine-structural differences of the alkylbenzenes (Table 7) [30]. For the members of homologous series of alkylbenzenes the *dI/dP* values are virtually constant. For isomers, *dI/dP* value is smaller for is*o*- than for *n*-alkylbenzenes, they are larger for *ortho*-compounds than for *meta*- and *para*-isomers, and they are smaller for symmetrical 1,3,5-compounds than for asymmetrical 1,2,3-isomers. There are sufficient indications that the relationships that exist between fine-structural differences of alkylbenzenes and *dI/dT* values are similar to that for *dI/dP* values.

Table 6

The influence of the type and pressure of the carrier gas on the retention indices of hydrocarbons on squalane (May & Baker)

Compound	I_{70}^{S}			*ΔI*	
	0.4 MPa	*0.4 MPa*	*0.26 MPa*	*N_2 - H_2*	*H_2*
	H_2	*N_2*	*H_2*	*(0.4 MPa)*	*(0.4-0.26 MPa)*
Benzene	641.51	641.96	641.45	0.45	0.06
Cyclohexane	667.14	667.46	667.02	0.32	0.12
o-Xylene	874.17	874.64	874.10	0.47	0.07
1-Octyne	783.52	783.60	783.52	0.08	0.00
2-Octyne	843.45	843.60	843.46	0.15	-0.01
3-Octyne	819.28	819.37	819.29	0.09	0.01
4-Octyne	812.50	812.59	812.51	0.09	-0.01

Table 7

Changes in retention indices of alkylbezenes on TCEP with changes in temperature, pressure and nature of carrier gas.

Alkylbenzene	dI/dT	dI/dP	dI
	(1 °C)	(0.1→0.2 MPa, N_2)	(H_2→N_2, 0.1 MPa)
toluene	2.0	1.0	1.7
1,4-xylene	2.1	0.7	1.3
isopropylbenzene	2.1	0.9	1.2
n-propylbenzene	2.2	1.0	1.1
1,2-xylene	2.4	1.2	1.2
1-methyl-4-ethylbenzene	2.4	1.0	1.1
1-methyl-3-isopropylbenzene	2.1	0.9	0.7
1-methyl-4-isopropylbenzene	2.1	0.9	1.3
1-methyl-2-ethylbenzene	2.4	1.2	1.2
1,3-diethylbenzene	2.2	1.1	1.1
1-methyl-2-isopropylbenzene	2.3	1.1	1.3
1,3-dimethyl-5-ethylbenzene	2.2	0.9	1.2
1-methyl-4-tert-butylbenzene	2.1	1.2	1.2
1,2-diethylbenzene	2.3	1.2	1.5
1,2,3-trimethylbenzene	2.7	1.5	1.3
n-pentylbenzene	2.4	1.4	1.1
1,3-dimethyl-2-ethylbenzene	2.6	1.3	1.2
1,2-dimethyl-3-ethylbenzene	2.7	1.3	1.3
1,2,4,5-tetramethylbenzene	2.7	1.3	1.1
1,2,3,5-tetramethylbenzene	2.8	1.3	1.1

4.2. Structure-retention relationships

4.2.1. Homomorphy factor

The calculation methods of hydrocarbon retention indices using molecular structure descriptors, quantum chemical, connectivity and topological parameters [33-37] for identification of isomeric hydrocarbons in complex mixtures are not adequately precise (in average ± 7 i.u.). The precise and reproducible retention indices are required for the retention structure relationships as the mean of analyte identification. Because the homology and isomerism are characteristic properties of hydrocarbons, the structural-retention relationships on homologous series are most interesting. The most suitable characteristic is homomorphy factor, *H,* defined as the difference of retention indices of the analyte and *n*-alkane with analogous carbon skeleton [38]. Thus value *H* characterizes contribution of the functional group to retention index. On the difference to the proclaimed linear dependence $I = f(C_z)$ for homologues, the *H* values in homologous series exhibit characteristic non-linear asymptotical decreasing dependence on the number of carbon atoms of homologous C_z, the decrease of *H* values is apparent at about seven carbon atoms from the beginning of the given structural trait [15-17]. The dependence $H = f(C_z)$ for particular homologous series of *n*-alkenes, prepared by catalytic dehydrogenation of C_6-C_{14}

n-alkanes, is given on Fig. 14. On the basis of regularity of these dependences by their extrapolation a relatively precise (better as 1 i.u.) prediction of the retention of higher homologous is possible. For isomers with new structural trait, in the case of *n*-hexadecenes for *trans*-8- and *cis*-8-hexadecene, the values *H* were obtained by extrapolation of *H* values for first homologous members with structurally new traits, it means for *trans-8-hexadecene* from *H* data for *trans*-3-hexene, *trans*-4-octene, *trans*-5-decene, *trans*-6-dodecene and *trans*-7-tetradecene and correspondingly for *cis*-8-hexadecene (Fig. 15). Similar dependences were used for the prediction of retention of the second, third, fourth, etc. members of the homologous series.
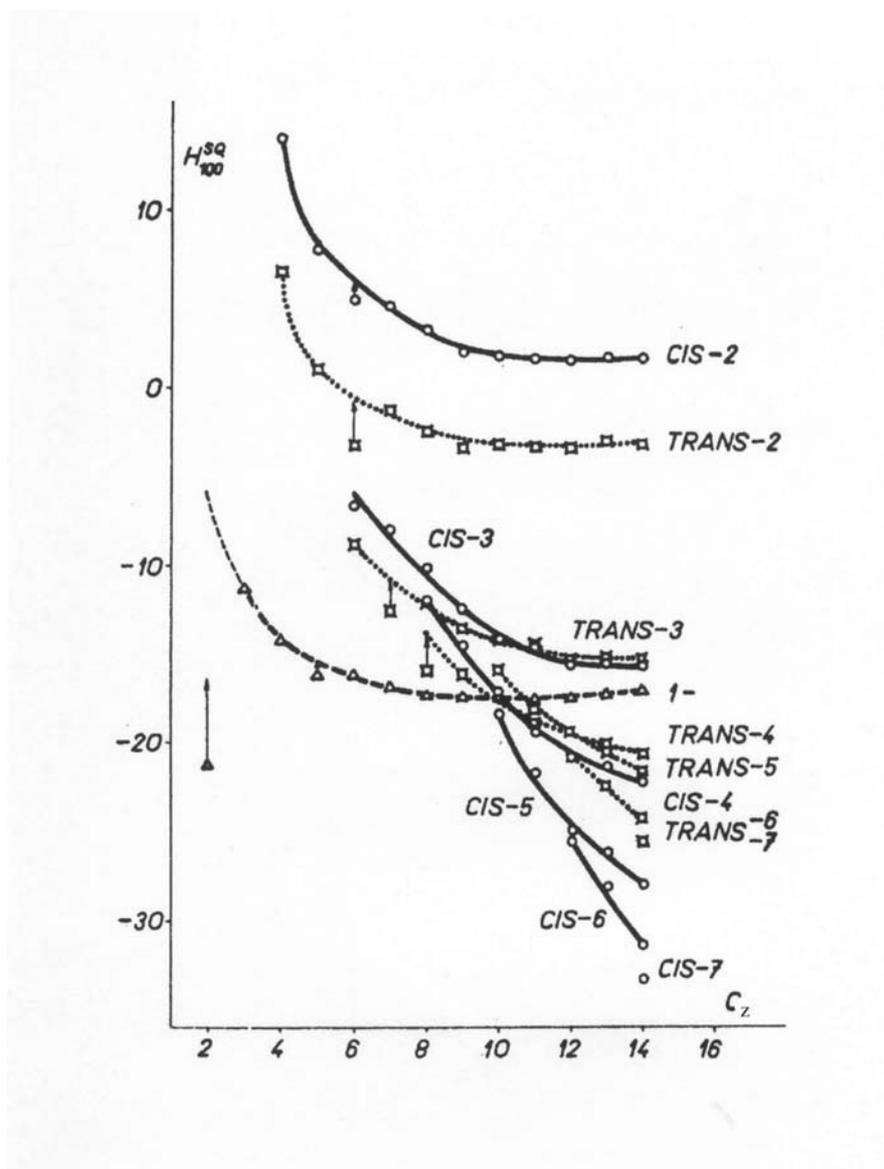
Fig. 14. Dependence of homomorphy factors H_{100}^{S} on carbon number for homologues series of *n*-alkenes on squalane at 100°C.
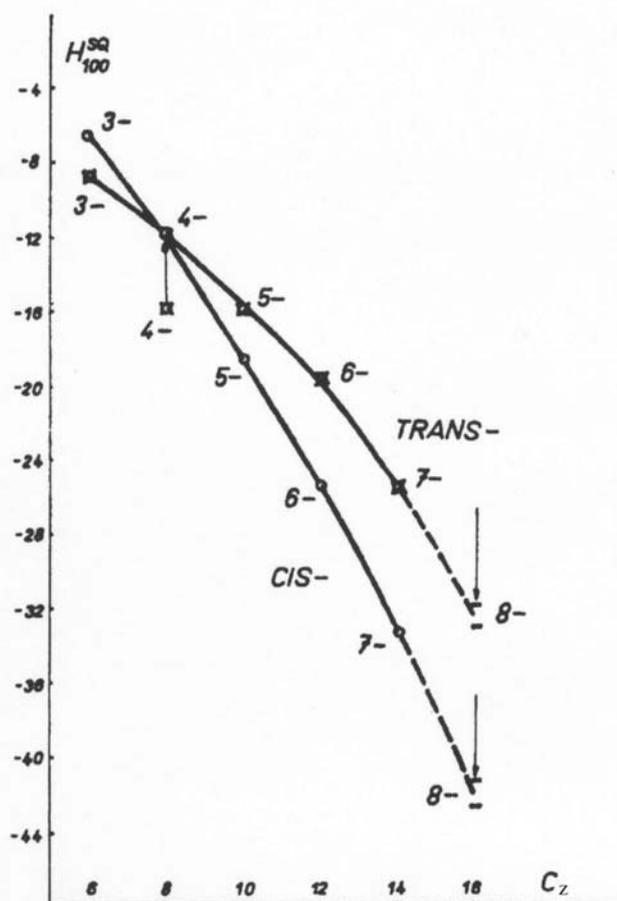
Fig. 15. Extrapolation of the retention positions of structurally new isomers of *n*-hexadecenes from the first members of homologous series with structurally new traits.

4.2.2 Propyl effect

The dependence on Fig. 14 allowed to discover anomalous retention behaviour of some homologous [15, 16, 39]. It can be seen the values *H* for 1-pentene, *trans*-2-hexene, *trans*-3-heptene, *trans*-4-octene and other *trans*-4-alkenes are lower in comparison with the values resulting from the regularity of the dependence $H = f(C_z)$ for corresponding homologous series. The reason is the structural arrangement of these congeners, which allows the forming of a suitable ring conformation of the propyl group with π-electron system that permits intramolecular orbital interactions, the multiple effects occur with structures involving several propyl groups:
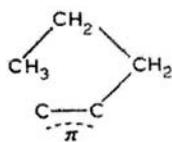
It occurs with all types of unsaturated hydrocarbons as well as with compounds in which carbon atoms forming part of a π-electron system are replaced by a heteroatom and those having a stretched cyclic structure. This phenomenon was called the propyl effect [40, 41].

Theoretically, an intramolecular hydrogen bridge between the π-electron system of a molecule as a proton acceptor and the methyl group showing a weak acidity is possible. It was found by consideration of molecular orbitals and use of the valency force field method that a common feature of 1-alkenes and *trans-n*-alkenes is that they have, as well as a double bond, one *syn*-allyl hydrogen atom. At that same time, a methyl group can approach the double bond only in 1-pentene, *trans*-2-hexene, *trans*-3-heptene, *trans*-4-octene and other *trans*-4-alkenes, i.e. in structure in which the propyl effects occurs. This assumption is confirmed by the fact that if the formation of a cyclic conformation is restricted for steric reasons, this effect does not occur e.g. with *cis*-alkenes (or ortho-dialkyl derivatives of *n*-propylbenzene).
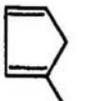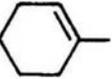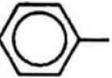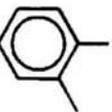
Basing on the interpolation of the dependence $H = f(C_z)$ for homologues, the contribution of the propyl
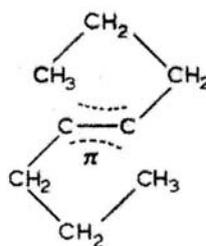
effect to the retention index was determined, expressed in terms of the difference between the measured and the interpolated values of the retention index of the particular analyte. The retention indices for various π-electron systems of hydrocaxbons separated on squalane are lower by -1 to -5 i.u., in the case of twofold propyl effect to -10 i.u. (Table 8). These values characterize the suppression of the solut-solvent interactions owing to steric hindrance due to the formation of the cyclic conformation. Lower retention of structures with the propyl effect can be explained on the basis of the dependence of the physicochemical properties of compounds on their conformation. In comparison with straight-chains the s*o*-called puckered structures, which include also structures with the propyl effect, show lower densities, refractive indices, melting and boiling points and weaker van der Waals interactions [42]. From the relationship between retention indices and boiling points follows that for example, the boiling point of *n*-propylbenzene due to assertion of propyl effect is about 1°C lower.

Table 8

The contribution of the propyl effect for retention index of different types of hydrocarbons analyzed on squalane at 70 °C

π-electron system	Hydrocarbon	Contribution (I.U.)
$CH_2=CH-$	1-Pentene	−1.0
$CH_3-CH=CH-$	trans-2-Hexene	−2.8
$C_2H_5-CH=CH-$	trans-3-Heptene	−1.6
$-CH=CH-$	trans-4-Octene	−3.5*
$HC\equiv C-$	1-Pentyne	−1.5
$CH_3-C\equiv C-$	2-Hexyne	−3.7
$C_2H_5-C\equiv C-$	3-Heptyne	−3.0
$-C\equiv C-$	4-Octyne	−4.0*
$C=C-C-C-C-C=C-$	1,trans-6-Decadiene	−2.0
$-C=C-C=C-$	trans-4,trans-6-Decadiene	−5.3*
	1-Propyl-1-cyclopentene	−4.7
	1-Propyl-1,3-cyclopentadiene	−5.3
	2-Propyl-1,3-cyclopentadiene	−5.2
	5-Propyl-1,3-cyclopentadiene	−5.1
	1-Propyl-1-cyclohexene	−5.0
	n-Propylbenzene	−5
	1,2-Dipropylbenzene	−10*

* Double propyl effect.

The contribution of propyl effect to the retention depends on the polarity of stationary phase. For example, for n-propylbenzene with increasing polarity of the stationary phase squalane, acetyltributylcitrate, triscyanoethoxypropane the values of contribution are -4.8, -5.6 and -11.0 i.u., respectively. It follows that the anomalous conformer has a lower gas chromatographic polarity than the corresponding hypothetical hydrocarbon with non anomalous structure. This result can be explained by hindering effects of the twisted propyl group on the polar solut-solvent interactions.

The most marked demonstration of the propyl effect is given by the separation of isomers with similar physico-chemical characteristics. For instance, the elution of *trans*-4- before *trans*-5-decene [15, 16] and of 4-decyne before 5-decyne [13] on nonmesogenic phases are unique cases where the isomer with the multiple bond closer to the end of the carbon chain is eluted before the isomer with the multiple bond positioned more internally. The formulation of the propyl effect in structure-retention dependence plays a significant role since it concerns a considerable number of compounds, e.g. of 192 *n*-alkadienes up to C_{11} [43] 15 % of the possible congeners exhibit the propyl effect. The formulation permits the explanation of deviations from regularity of structure-retention dependences and thereby also the identification of such anomalous compounds purely by gas chromatographic means. The propyl effect was not known in theoretical organic chemistry. It was formulated on the basis of gas chromatographic measurements and on the generalization of anomalies observed in retention-structure relationships. Gas chromatography thus served as an indicator of fine structural peculiarities in the structure of homologues and stimulated their further study with methods of structural chemistry [41].

The propyl effect influences the regularity of all reten-tion-structure relationships related to the number of carbon atoms in the molecule or to the position of the functional group. In the case of *n*-alkadienes, the regularity of reten-tion-structure relationships can be affected also by structural effects as conjugation, hyperconjugation, homoconju-gation, alternation, σ-overlapping of *p*-orbitals [41, 43]. Fig. 16 shows a schematic illustration of the influence of these structural effects on the retention of *n*-alkadienes in homologous series. Conjugation, hyperconjugation, homoconjugation and alternation cause higher retention values of alkadienes. On other hand, σ-overlapping of *p*-orbitals and the propyl effect result in their lower retention. These effects are expressed as a contribution to a hypothetical retention index of *n*-alkadienes on squalane phase at 70 °C. In some cases, also the combination of individual structural effects was observed, e.g. with 2,5-heptadienes both homoconjugation and double hyper-conjugation occurs and therefore their retention is almost as high as that of conjugated 1,3-heptadienes. The dependence of $H = f(C_z)$ for all C_5-C_{10} *n*-alkadienes with conjugated and isolated double bonds is presented in Fig. 17. The mixtures of alkadienes were obtained by catalytic isomerization of α,ω-alkadienes, resp. as by-products of catalytic dehydrogenation of *n*-alkanes.
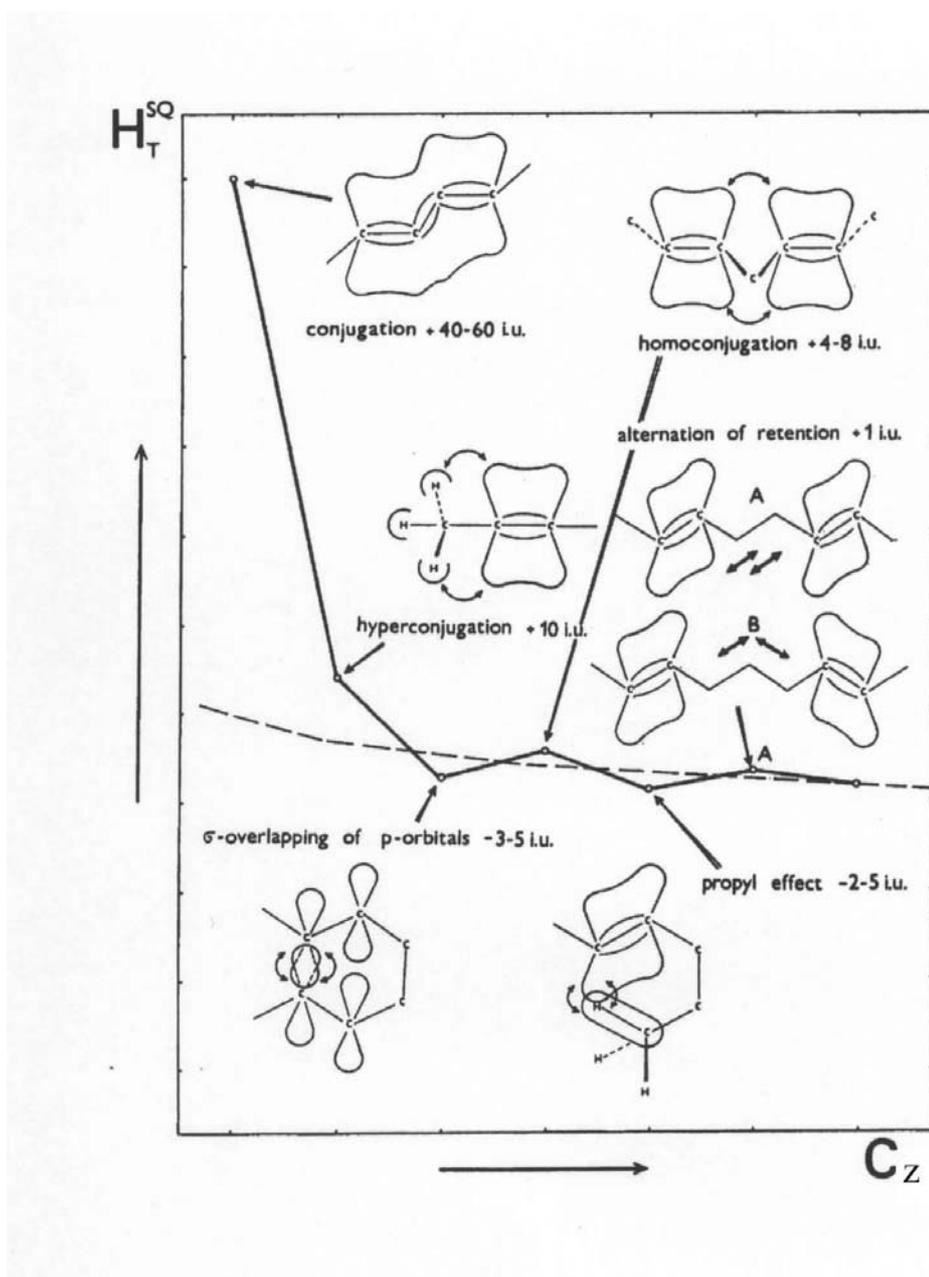
Fig. 16. Schematic illustration of the influence of various structural effects on the homomorphous factor of *n*-alkadiene homologues on squalane at 70°C.

Fig. 17. Dependence of the homomorphy factors on the number of carbon atoms for C_5-C_{10} *n*-alkadienes on squalane at 70°C.

Further structural effect resulting in lower retention is the presence of a quaternary or tertiary carbon atom near the end of the carbon chain which was observed for branched alkanes [3], alkenes [44,45] and alkynes [46]. A higher symmetry of the molecule and hence also lower polarizability and weaker solute-solvent interactions are characteristic for these structures. From Fig. 18 can be seen that in connection with this effect retention of 6-methyl-1-heptene is lower than of 5-methyl-1-heptene.
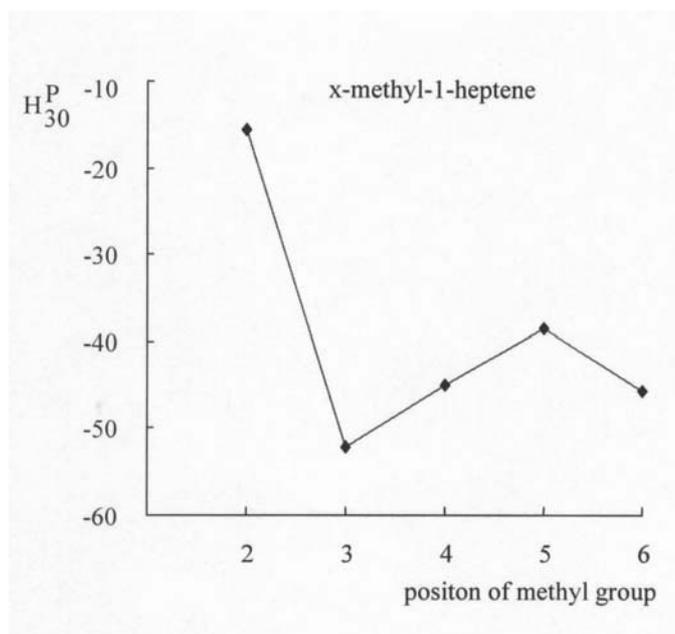

Fig. 18. Dependence of the homomorphy factors on the position of methyl group for *x*-methyl-1-heptenes separated on polydimethylsiloxane at 30°C.

4.2.3. Correlation of retention indices on two stationary phases

The dependence of retention data on the polarity of stationary phase is usually employed for the identification of analytes with different functional groups. For the identification of isomers this approach is difficult. A certain resolution of isomers and congeners of C_6-C_{15} alkylbenzenes was obtained by correlating their retention indices on squalane and high-polar TCEP as stationary phases [47]. This relationship is shown in Fig 19. Alkylbenzenes with the same number of carbon atoms can be distinguished by characteristic half-ellipsis with flat bases. For isomeric alkylbenzenes a dependence on the size and position of the alkyl groups can be seen, as demonstrated by the schematic representation for all isomeric C_{10} alkylbenzenes.
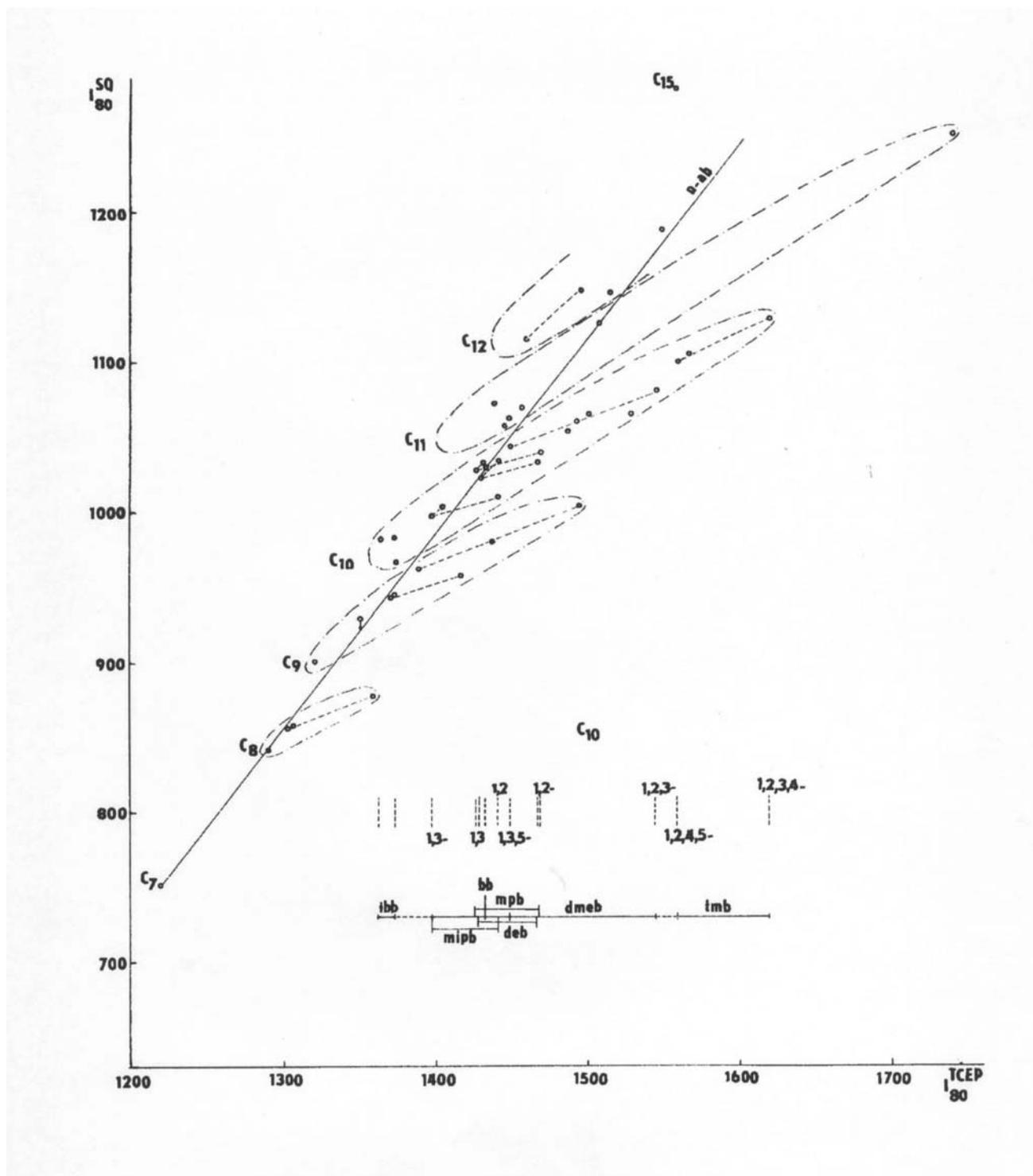
Fig. 19. Dependence of the retention indices of alkylbenzenes on squalane *versus* those on 1,2,3-triscyanoethoxypropane at 80°C; b – benzene and butyl, d - di, e - ethyl, i - iso, m - methyl, p - propyl and t - tetra.

4.2.4. Boiling point vs. retention index

One of the correlations between molecular structure and gas chromatographic retention of analytes is the correlation between boiling point and retention index [48-51]. The unknown boiling points of *n*-alkenes up to C_{16} were correlated from the measured retention indices on squalane as stationary phase. The method is based on proportionality coefficients k_p expressing the ratio of differences of the boiling points, δT_b, and the retention indices, δI, of two isomers $k_p = \delta I / \delta T_b$, and also on the dependence of these coefficients on the number of carbon atoms, the structure of the isomers and the column temperature (Table 9). The boiling points of *n*-alkenes T_{bx} were calculated from equation [48].

$$T_{bx} = T_b + \left(\delta I / k_p \right),$$

Table 9

Dependence of the proportionality coefficients k_p on the number of carbon atoms for pairs of isomeric alkenes at 86 °C on squalane

Number of carbon atoms	*trans*-2-/1-	*trans*-3-/1-	*cis*-2-/l-	*cis*-3-/1-
		alkene		
6	3.1	2.3	4.0	3.3
7	3.7	2.3	4.5	4.2
8	4.1	3.0	4.7	4.4
9	4.7	3.4	*5.0*	4.2
10	5.2	3.7	*5.3*	3.9
11	5.8	4.0	*5.6*	3.6

where T_b is the boiling point of the reference 1-alkene or other reference alkene isomer. The reproducibility of the boiling points of individual *n*-alkenes up to C_{13} calculated from different reference isomers or column temperatures was on an average ± 0.1°C. Less precise values were found by correlation of isomers with very close boiling points, e.g. in the case of the *cis-trans* isomers of some *n*-alkenes for which an inverse sequence of retention was observed within markedly narrow temperature limits (30°C). The equation was proposed for the correlation between boiling points and retention indices taking into account the effect of differences in activity coefficients (γ) of hydrocarbons as well as the temperature dependence of vapour pressures (p^0) and activity coefficients [50], with better agreement than one index unity:

$$\delta I = K \delta T_b - \frac{K}{k_2} . log\left(\gamma_2 / \gamma_1 \right).$$

In this equation $K = -100k_2 / log\ \alpha'; \alpha' = t'_{R,z+1} / t'_{R,z}$ being the separation factor of the *n*-alkanes between which the pair of hydrocarbons is eluted, and $k_2 = log\ \dfrac{p_2^0}{p_1^0} / \left(T_{b2} - T_{b1} \right)$

4.2.5. Logarithmic vs. linear retention data

On the basis of high-precision measurements of the retention of benzene and 47 alkylbenzenes C_7-C_{15} on three stationary phases of different polarity, the accuracies of the determination of linear and logarithmic retention indices were compared, and the correlations between the structure and the retention of alkylbenzene congeners of these two interpolation characteristics were evaluated [52]. The linear retention index can be measured more accurately than the logarithmic value. Fine correlations between structure and retention are different for these two types of retention indices.

On Fig. 20 the dependence of the difference of values of logarithmic, *I,* and linear retention indices, *J,* of alkylbenzenes vs. logarithmic retention indices of alkylbenzenes on squalane at 80.8°C is presented. Fig. 21 demonstrates the dependence of the difference of retention logarithmic and linear indices temperature coefficients on logarithmic retention index on squalane at 80.8 °C for alkylbenzenes. From these figures follows that the logarithmic retention indices are more suitable for these correlations. The differences are due to the fact that for structural correlations of linear retention indices the dependence of the position of the peak maxima of the analyte between two neighbouring *n*-alkanes must also be considered. As the relationships between structure and linear retention indices are more complicated than those of logarithmic retention indices, the logarithmic interpolation characteristics are more suitable when using the correlation between structure and retention as a means of identification.
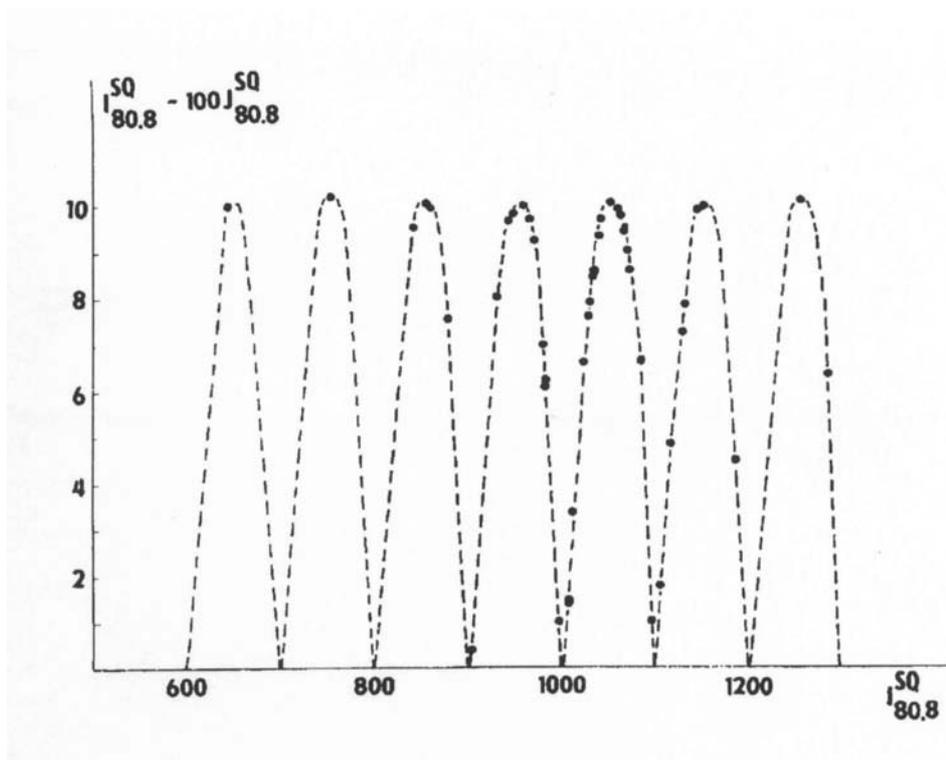

Fig. 20.   Dependence of the difference $I^{S}_{80.8} - 100.J^{S}_{80.8}$ on $I^{S}_{80.8}$ for alkylbenzenes.
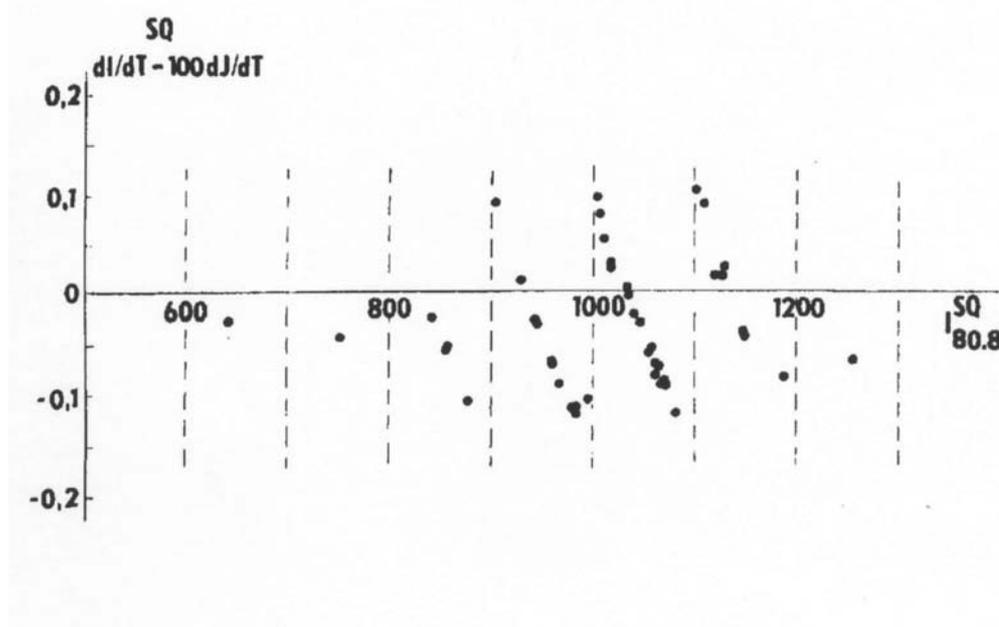
Fig. 21. Dependence of the difference $dI^S / dT - 100.dJ^S / dT$ on $I_{80.8}^S$ for alkylbenzenes.

4.3. Hyphenated spectrometric techniques

The identification of gas chromatographic separated analytes only on the basis of the retention data is not positive. The chromatographic identification should be confirmed by positive identification method such as mass spectrometry or Fourier transform infrared spectrometry. The possibilities of their use for the identification of isomeric alkenes were illustrated in the analysis of all isomeric *n*-nonadecenes[9]. The separation of all isomers in columns with Apolan and liquid crystalline stationary phase PrBHP and their identification on the basis of mentioned dependences $H = f(C_z)$ were obtained. Tabulated mass and infrared spectra for comparison with measured spectra were unknown. The measured mass spectra of chromatographic peaks identified as *cis-* and *trans-* isomeric *n*-nonadecenes were very similar in agreement with the fact that mass spectrometry does not permit to differentiate *cis-* and *trans-*isomers. However, the infrared spectra of the *cis-* and *trans-* isomers are distinctly different. The IR spectra for *trans-*2-isomer showed characteristic absorbance under the wave number 963 cm⁻¹. The characteristic absorbance 967 cm⁻¹ was measured for 3- till 9-positional *trans-*isomers. It means that the IR spectra do not allow to differentiate between positional *trans-*3- and other *trans-*isomers with more inner double bond. The difference of absorbance of *trans-*2-isomer and other *trans-*positional isomers is probably in connection of the assertion to the hyperconjugation effect of *trans-*2-isomer.

For obtaining retention indices of some isomeric hydrocarbons unseparated by capillary gas chromatography the mass spectrometric deconvolution was applied. All isomeric acyclic alkenes C_7-C_8 were mass spectrometrically inspected using data of library and own spectra measurements of prepared alkenes [40,45]. Retention times of some gas chromatographically unseparated pairs of isomer were obtained by their mass spectrometric deconvolution using the specific single ion monitoring. In such way, the index difference of two isomers 0.03 i.u. was found, whereas the resolution ability of used gas chromatographic separation system was approximately 1 i.u. On Fig. 22 GC-MS-SIM chromatogram of acyclic octenes from fluid catalytic cracked gasoline is given obtained by separation in 150 m x 250 p.m x 1.0 p.m capillary coated with polydimethylsiloxane as stationary phase. It can be seen that from 93 possible octenes 16 isomeric pairs are chromatographically not separated. The difference in abun-

dance of some specific single ions of isomers allows mass spectrometric deconvolution of 12 isomeric pairs; the deconvolution of non separated triple acyclic octene isomers is documented on Fig. 23. Primarily, the presence of all 59 acyclic C_5-C_7 alkenes and 81 octenes in fluid catalytic cracked gasoline was determined.
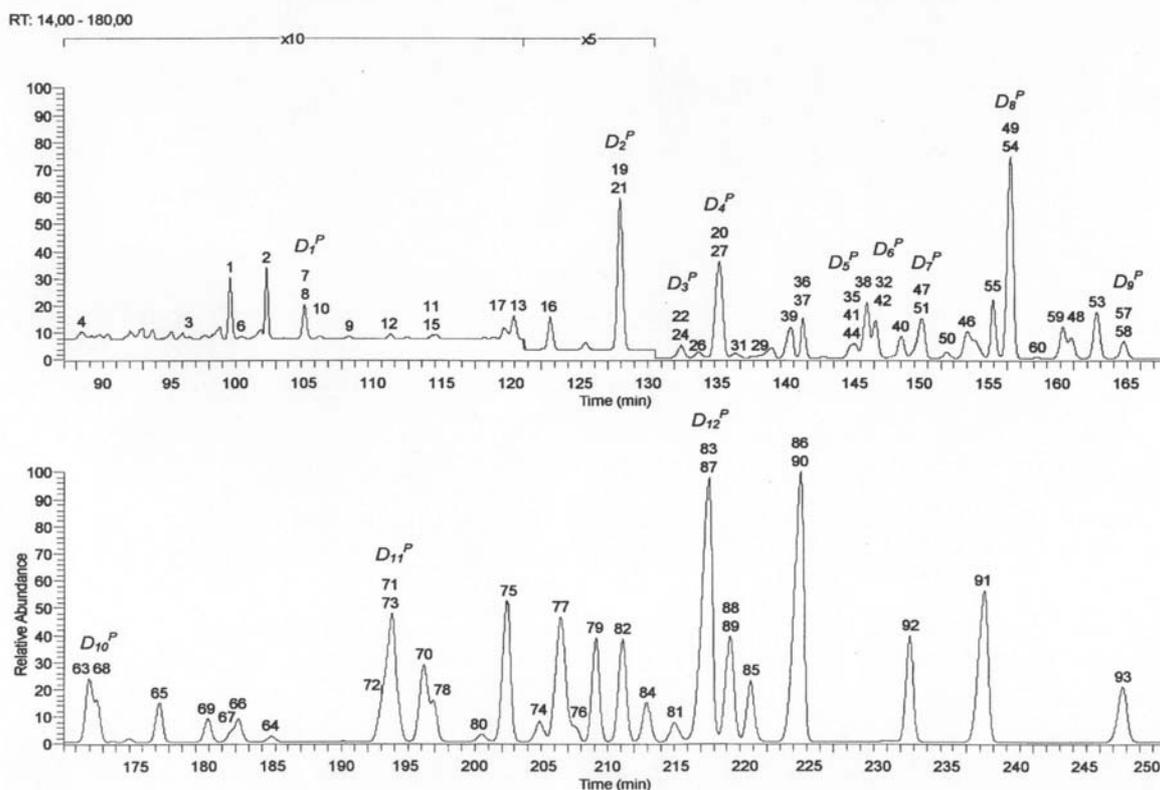

Fig. 22. GC-MS/SIM chromatogram of separation of acyclic octenes from the fluid catalytic cracked gasoline on PDMS column (150 m x 250 μm x 1.0 μm, Supelco) at 30°C; $D_1^P - D_{12}^P$ - mass spectrometric deconvoluted peaks.
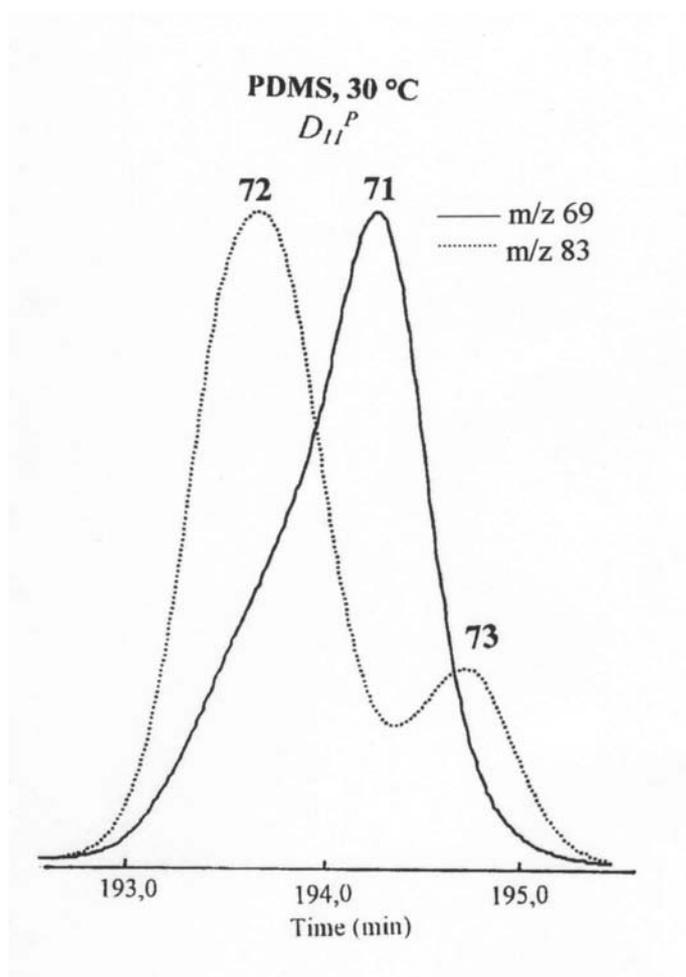
Fig. 23. Mass spectrometric deconvolution of gas chromatographic unseparated triplet octene isomers on the PDMS column at 30°C (D_{11}^P - see   Fig. 22); 71 - 4-methyl-*cis*-3-heptene, 72 - 2-methyl-1-heptene, 73 - 5-methyl-*cis*-2-heptene

5. Conclusions

The similarities in the properties of isomeric hydrocarbons and the complexities of their mixtures lead to capillary gas chromatography as the most promising method for their total analysis. The possibilities of the separation and identification of isomeric hydrocarbons by the contemporary means of capillary gas chromatography with hyphenated spectrometric techniques are essentially extended. The unique separations of positional isomers, including isomers with functional group in the middle of the carbon chain with new structural trait which are most difficult separable isomers, as well as, of *cis-trans*- isomers, and of diastereoisomeric hydrocarbons can be achieved by separation systems combining the high efficiency of capillary column with isomeric selectivity of liquid crystals as stationary phases. The possibilities of identification on the basis of published retention indices were improved by considering the interface adsorption effects in capillary gas-liquid chromatography. The no*n*-linear structure-retention correlations in fine structure of homologous series of hydrocarbons, mainly the dependence of homomorphy factor on number of carbon atoms of analytes by extrapolation enable the precise prediction of retention of higher molecular isomers or congeners supposing that fine structural effects, inclusive propyl effect, are considered. For confirmation of identifica-

tion mainly of *cis-trans* isomers also precise *dl/dT* values can be useful.

The mass and infrared spectra of isomeric hydrocarbons can also be quite similar leaving the retention index system as the basic alternative for their identification. However, in some cases, the mass spectra of isomeric hydrocarbons are different and allow the deconvolution of gas chromatographically unseparated isomers. The FTIR spectra are suitable for distinguish of *trans-* from *cis-* isomers, but they do not allow a differentiation between positional isomers.

On the basis of the precise measurement of Kováts retention indices of approximately 1000 hydrocarbons and their correlation with molecular structure on apolar, polar and liquid crystalline stationary phases, certain regularities in retention behaviour of alkanes [2, 18], alkenes [7, 16, 17], alkynes [13, 46], alkadienes [43], cycloalkanes [53], cycloalkenes and cycloalkadienes [54] and aromatic hydrocarbons [29, 30, 47, 55, 56] were formulated.

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