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Separation and identification of all isomeric *n*-nonadecenes by capillary gas chromatography on a mesogenic stationary phase with Fourier transform infrared and mass spectrometric detection

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ABSTRACT

High-resolution capillary gas chromatography (HRGC) with an isomeric selective liquid crystal as stationary phase permits a better separation of the seventeen possible *n*-nonadecene isomers and *n*-nonadecane than a separation system with a non-mesogenic stationary phase. For the identification of the separated isomers, structure–retention correlations based on extrapolation of the dependence of homomorphous factors on the number of carbon atoms for homologous series of *n*-alkenes and the different temperature dependences of the retention indices of geometrical isomers were used. Identification was confirmed by a combination of HRGC with Fourier transform infrared and mass spectrometric detection on the basis of infrared spectra which are distinctly different for the geometrical isomers. The rule of the alternation retention of *cis*- and *trans*-alkenes with an odd number of carbon atoms separated on a mesogenic stationary phase was reformulated.

INTRODUCTION

n-Alkenes represent an interesting model for the study of gas chromatographic (GC) isomeric selectivity concerning positional and geometrical isomerism. They are also technologically important materials obtained as complex mixtures of isomers by catalytical dehydrogenation of *n*-alkanes with a wide range of carbon numbers.

In GC separations of higher *n*-alkenes, a favourable effect of the polarity of stationary phase is compensated for by the interfacial adsorption of isomers on the polar stationary phase–gas interface, this effect being inversely proportional to the polarity of the individual isomers [1]. Separation systems combining the high efficiency of capillary columns with the isomeric selectivity of liquid crystals as stationary phases permit improved separations of complex mixtures of isomers, including those with very similar physico-chemical properties [2].

In previous work [3], the separation of isomeric C_{17} and C_{18} *n*-alkenes and *n*-alkanes was studied on a high-efficiency capillary column with 4′,5-*n*-hexylpyrimidin-2-yl-phenyl 4-*n*-propylbenzoate (PrBHP) liquid crystal as stationary phase. The separation was optimized with respect to the stationary phase film thickness and column temperature. This separation system permits better and faster separa-

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tions of isomeric *n*-heptadecenes and *n*-octadecenes compared with previously obtained separations on non-mesogenic and mesogenic stationary phases.

The aim of this work was the separation and identification of all isomeric *n*-nonadecenes and *n*-nonadecane using the separation system with PrBHP liquid crystal as stationary phase coupled with Fourier transform infrared (FT-IR) and mass spectrometric (MS) detection. The contribution of the mesogenic stationary phase used to the separation of isomeric *n*-nonadecenes is based on a comparison with their separation on the non-mesogenic phase Apolane-87 in a capillary column with an efficiency of about 500 000 plates [4].

EXPERIMENTAL

As a model mixture, the product of the catalytic dehydrogenation of *n*-nonadecane, in which the *n*-alkene content was enriched by displacement liquid chromatography with 2-propanol, was used. It contains a mixture of the seventeen possible isomeric *n*-nonadecenes and *n*-nonadecane.

GC measurements were carried out with a Hewlett-Packard GC–FT-IR–MS system. The model mixture was separated in a glass capillary column with liquid crystalline PrBHP (synthesized by Dr. K. D. Scherf, Martin-Luther University, Halle, Germany) as stationary phase, having a mesophase range from 65 to 170°C and possible supercooling to about 28°C. The capillary column was prepared from Unihost glass (Kavalier, Teplice, Czechoslovakia). After etching with gaseous hydrogen chloride, the glass capillary was coated statically with a solution of PrBHP in dichloromethane. The effective efficiency of a prepared column of 90 m × 0.25 mm I.D. for the studied compounds was about 200 000 plates (film thickness 0.03 μm, column temperature 100°C, average linear velocity of carrier gas 40 cm s^{-1}). The selectivity coefficient (relative retention), α, for *p*- and *m*-xylene at 50°C was 1.16.

RESULTS AND DISCUSSION

The chromatograms of isomeric *n*-nonadecenes and *n*-nonadecane obtained with the PrBHP liquid crystal separation system and those obtained with Apolane-87 (from Ref. 4) are shown in Fig. 1. Retention indices and their temperature coefficients of

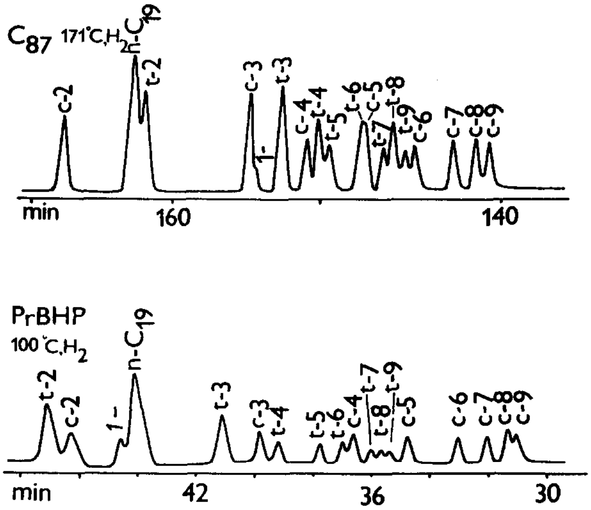


Fig. 1. Separation of isomeric *n*-nonadecenes and *n*-nonadecane using a 90 m × 0.25 mm I.D. column with PrBHP (*N* ≈ 200 000 plates) and a 200 m × 0.25 mm I.D. column with Apolane-87 (*N* ≈ 500 000 plates). c = *cis*-; t = *trans*-; 1 = 1-nonadecene; n-C_{19} = *n*-nonadecane.

TABLE I

RETENTION INDICES OF *n*-NONADECENES AND THEIR TEMPERATURE COEFFICIENTS ON PrBHP AT 100°C AND ON APOLANE-87 AT 170°C

dI^{PrBHP}/dT values were measured within the temperature range 90–100°C and $dI^{Ap\text{-}87}/dT$ values within the range 170–190°C.

n-Nonadecene	I_{100}^{PrBHP}	dI/dT	$I_{170}^{Ap\text{-}87}$	dI/dT
cis-9-	1839.2	0.57	1860.3	0.12
cis-8-	1840.4	0.50	1861.7	0.12
cis-7-	1844.8	0.51	1864.4	0.11
cis-6-	1850.3	0.48	1869.0	0.11
cis-5-	1859.1	0.42	1874.7	0.10
trans-9-	1862.1	0.39	1870.4	0.09
trans-8-	1863.5	0.37	1871.3	0.08
trans-7-	1865.2	0.33	1872.8	0.08
cis-4-	1868.3	0.37	1881.3	0.08
trans-6-	1869.9	0.30	1875.3	0.07
trans-5-	1873.7	0.29	1878.9	0.06
trans-4-	1880.1	0.23	1879.9	0.04
cis-3	1882.4	0.23	1887.9	0.06
trans-3-	1888.3	0.17	1884.6	0.01
1-	1902.0	0.07	1887.1	0.04
cis-2-	1908.3	0.24	1907.6	0.06
trans-2-	1910.9	0.10	1899.0	0.00

n-nonadecenes on PrBHP and Apolane-87 are given in Table I.

Individual *n*-nonadecene isomers were identified by extrapolation of the dependence of the homomorphy factors, *H*, on the number of carbon atoms (n_c) for the homologous series of C_{15}–C_{18} *n*-alkenes, on the basis of previously measured retention indices [3]. The characteristic monotonous dependence of homomorphy factors, $H = f(n_c)$, for homologues on a non-mesogenic stationary phase does not apply on mesogenic stationary phases because it is influenced by the alternation of retention in homologous series when homologous with the orientation of the carbon chain more in the direction of the molecular axis have increased retention [3,5]. In connection with alternation of retention, in some instances an opposite retention order of isomers with the double bond in the middle of the carbon chain and their neighbouring positional isomers on mesogenic, in comparison with their separation on non-mesogenic, stationary phases has been found. Therefore, for the identification of isomeric *n*-nonadecenes separated on PrBHP, further means were used.

The identification of *cis* and *trans* isomers was confirmed on the basis of the different temperature dependences of their retention indices. The data in Table I show that the d*I*/d*T* values on PrBHP are higher for *cis* than for *trans* isomers by an average of 0.14 i.u./°C. On Apolane-87 the corresponding

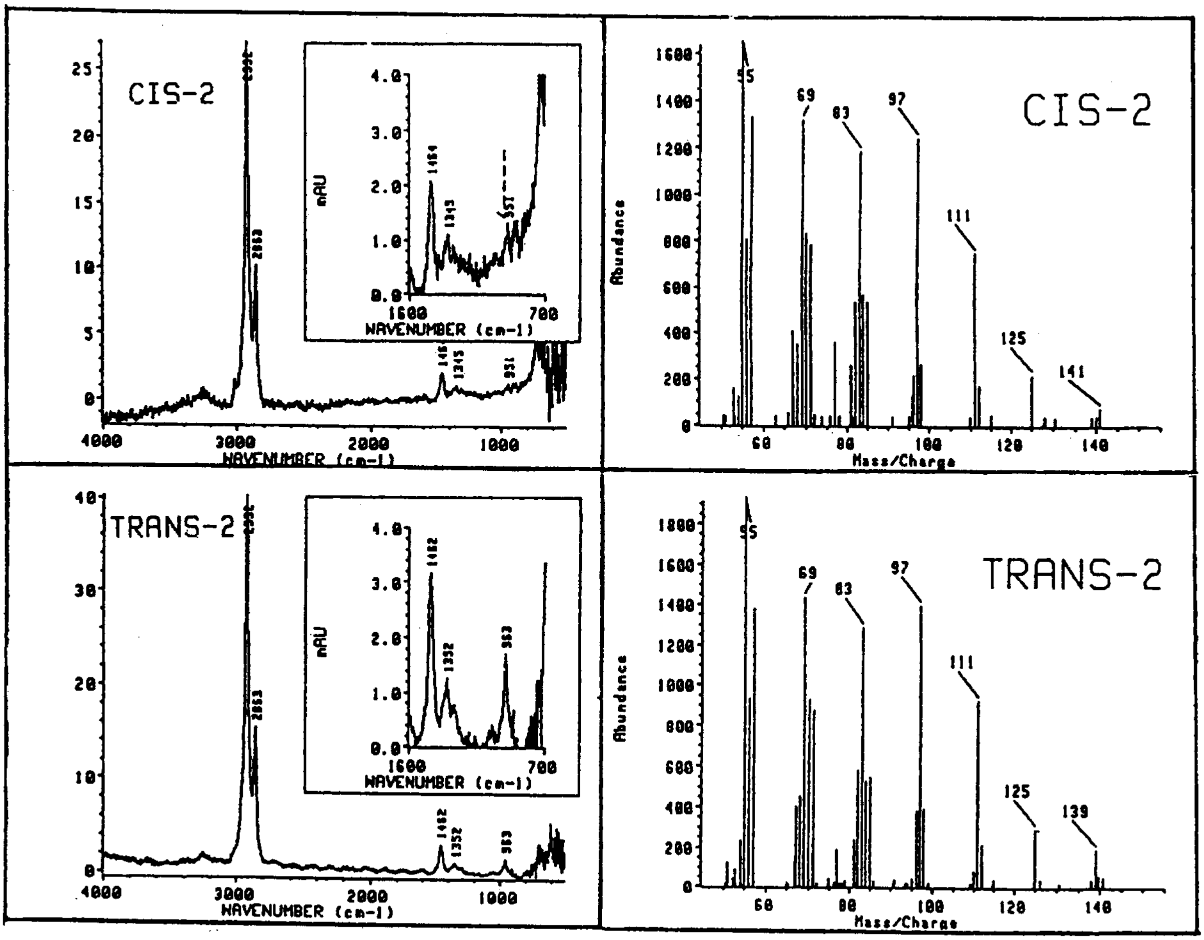


Fig. 2. Mass and IR spectra of *cis*-2- and *trans*-2-nonadecene.

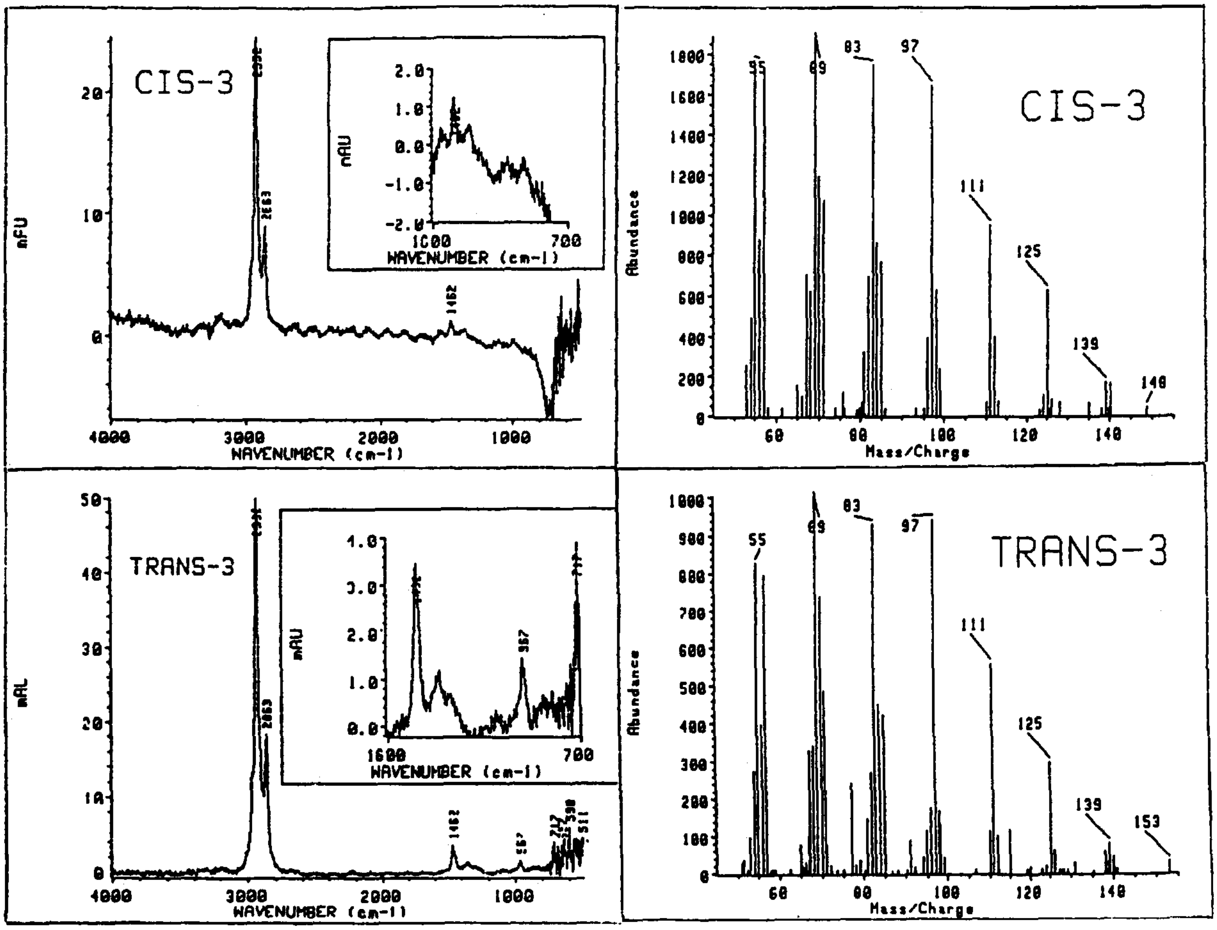


Fig. 3. Mass and IR spectra of *cis*-3- and *trans*-3-nonadecene.

difference is 0.05 i.u./°C; therefore, easier temperature optimization of their separation is possible on the PrBHP column.

The identification of isomeric *n*-nonadecenes carried out on the basis of structure–retention correlations was confirmed by FT-IR and MS detections of the eluates from the PrBHP capillary column. The results for the peaks identified as *cis*-2- and *trans*-2-nonadecenes and *cis*-3- and *trans*-3-nonadecenes are shown in Figs. 2 and 3, respectively. The geometrical and positional isomers of *n*-nonadecenes produce very similar mass spectra, and therefore their use for identification purposes is problematic. However, the infrared spectra of the geometrical isomers are distinctly different [6]. In contrast to *cis* isomers, the *trans* isomers show a characteristic absorption at 963 cm^{-1} for *trans*-2-nonadecene and at 967 cm^{-1} for *trans* isomers with the double bond located closer to the middle of the carbon chain of the molecule (*trans*-3- up to *trans*-9-nonadecene).

The dependence of the difference in the retention indices of neighbouring positional *cis*- and *trans*-*n*-nonadecene isomers (δI values) on the position of the double bond, in comparison with those obtained on Apolane-87, is shown in Fig. 4. The δI values of positional *cis* and *trans* isomers increase with a shift of the double bond from the middle to the end of the carbon chain. The δI values on PrBHP are generally higher, with the exception of

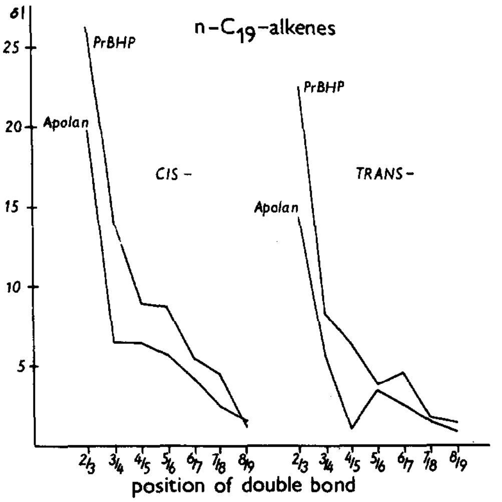


Fig. 4. Dependence of difference in retention indices of neighbouring positional *cis*- and *trans*-nonadecene isomers on the position of the double bond for PrBHP and Apolane-87.

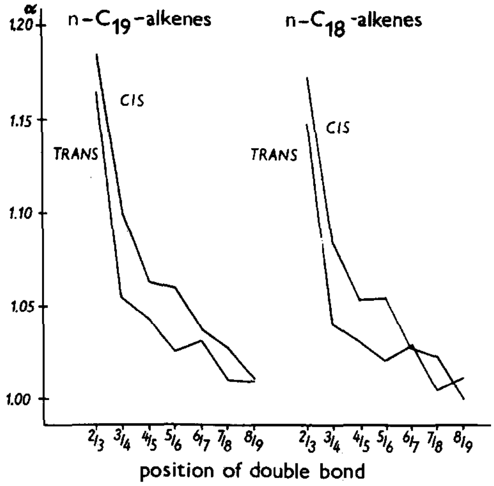


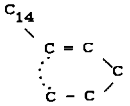
Fig. 5. Dependence of relative retention values on the position of the double bond for neighbouring positional *cis* and *trans* isomers of *n*-octadecenes and *n*-nonadecenes on PrBHP.

the pair *cis*-8–*cis*-9-nonadecene, even taking into consideration the different column temperatures used with PrBHP and Apolan-87. This is in agreement with the fact that the selectivity of liquid crystals for positional isomers increases with a shift of the double bond from the middle to the end of the carbon chain [5]. Hence the selectivity increases in the same direction as the retention of positional isomers, and therefore their separation is more favoured on a liquid crystal than on a non-mesogenic stationary phase. The comparison of the retention indices of *n*-nonadecenes measured on PrBHP and those measured on Apolane-87 shows a higher retention range of the studied compounds (66.1 i.u.) relative to Apolane-87 (47.3 i.u.). As is shown in Fig. 1, using a column with PrBHP the separation of all isomeric *n*-nonadecenes was achieved at a 2.5-fold lower efficiency in comparison with the Apolane-87 column.

The lower δI value for the pair *cis*-8-/*cis*-9-nonadecene on PrBHP than on Apolane-87 is connected with the alternation of retention of positional *n*-alkene isomers on mesogenic phases. From the data in Fig. 4, it follows that on a mesogenic phase *cis*-nonadecenes with an odd position of the double bond and *trans*-nonadecenes with an even position of the double bond show an increased retention, as follows from the regular decrease in retention with a shift of the double bond from the end to the middle of the carbon chain. However, previously [3,5], on the basis of results on alternation of retention for homologous series of *n*-alkenes on a mesogenic phase, the increased retention of *n*-alkenes with an odd number of carbon atoms for *cis*-alkenes with an even position of the double bond and for *trans*-alkenes with an odd position of the double bond was proposed.

The dependence of the relative retention values, α, on the position of the double bond for neighbouring position *cis*- and *trans*-nonadecenes and -octadecenes on PrBHP is shown in Fig. 5. It seems that trends of these dependences are similar to those in Fig. 4. This means that the alternation of the retention of *n*-alkanes (as standards in the Kováts retention index system) on PrBHP does not affect the trends of the alternation retention of positional *trans*- and *cis*-nonadecene isomers. These results and also similar results obtained for C_{13}, C_{15} and C_{17} *n*-alkenes confirm the formulated trends of alternation of the retention of *cis*- and *trans*-*n*-alkenes with an odd number of carbon atoms on mesogenic stationary phases. Previously formulated trends of alternation of retention of these *n*-alkenes were distorted by the effect of the alternation of retention of *n*-alkenes with an even number of carbon atoms in homologous series.

A low δI value was found on Apolane-87 for the pair *trans*-4-/*trans*-5-nonadecene (Fig. 4), the separation of which on Apolane-87 is worse than the separation of isomeric pairs of *trans*-nonadecenes having a more central position of the double bond in the carbon chain. This result is connected with the propyl effect experienced by the *trans*-4-isomer. The propyl effect is an intramolecular interaction between the propyl group and the π-electron system of the double bond [4,5]:



which causes a lower retention of this isomer of *ca.* 3 i.u. Therefore, this isomer is eluted more closely to the *trans*-5-isomer, as could be predicted from the regularity of the dependence of the retention of the positional *trans* isomers on the position of the double bond. On PrBHP in connection with alternation of retention, the increased retention of *trans*-4-nonadecene leads to the partial elimination of the effect of a propyl group on the retention dependence (see Fig. 4). It is evident from the measurements on Apolane-87 that the propyl effect is present also at relatively high temperatures, *e.g.* 190°C.

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