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SEPARATION OF MIXTURES OF ISOMERIC PERHYDROAROMATIC HYDROCARBONS ON CAPILLARY COLUMNS PACKED WITH GRAPHITIZED CARBON BLACK

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SUMMARY

Mixtures of stereoisomers of 1,2-cyclopentanodecalin, perhydrofluorene and perhydrophenalene are completely separated on capillary glass columns packed with graphitized thermal carbon black. These mixtures can be formed by catalytic hydrogenation of the corresponding aromatic hydrocarbons. The isomers elute from the column in order of the flatness of their molecules. Correspondingly, the components were identified on the basis of the geometric characteristics of their molecules and the retention indices of the isomers.

INTRODUCTION

In previous papers[1–4] the chromatographic separation of families of isomers of perhydroanthracene, perhydrophenanthrene, 1,2-cyclopentanodecalin, perhydrofluorene, perhydrophenalene and similar compounds was described. These compounds occur widely in oils and can be obtained by catalytic hydrogenation of the corresponding aromatic compounds. For example, hydrogenation of anthracene can give, depending on the conditions, isomers of perhydrophenanthrene in addition to the isomers of perhydroanthracene[5]. All these compounds are isomers of tricyclotetradecane, differing only in the junction of the rings (see formulae). By hydrogenation of fluorene under certain conditions the isomers of perhydrofluorene, 1,2-cyclopentanodecalin and perhydrophenalene can be formed, and they can isomerize further to give adamantane structure[5]. These compounds are also isomers of tricyclotridecane (see formulae).

It has been found[1–4] that the identification of the components even on chromatograms of the separate families is difficult, especially in gas-liquid chromatography[5,6]. With mixtures of isomers of different families the problem of their complete separation becomes more complicated. However, the use of effective capillary columns packed with graphitized thermal carbon black (GTCB) allowed the complete separation of all the isomers of families of such compounds, and also their identification because the retention of isomers on GTCB increases with increasing flatness of their molecules[7–9]. Using the relationship between retention on GTCB and molec-

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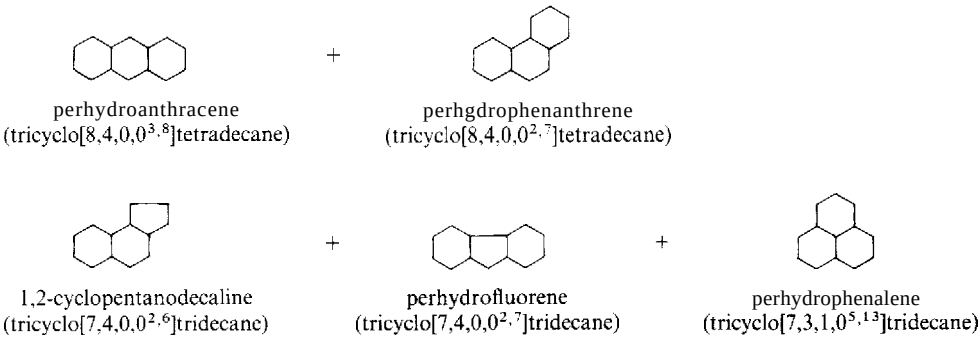


ular structure, the isomers of each family were identified and for each the Kováts retention indices, Henry constants at different temperatures and heats of adsorption were determined[1–4]. The determination of Henry constants at different temperatures is important for solving of the reverse molecular-statistical problem, i.e., for the calculation of some structural parameters of the molecules by the chromatostructural method (chromatoscopy[9]). For comparison, the retention indices of the isomers of these families were determined on a gas-liquid capillary column containing SE-30. The comparison of the results showed that the selectivity of separation of stereoisomers on GTCB is much higher. However, to achieve this high selectivity it is necessary to prepare high-efficiency columns packed with GTCB. In this work, using the sensitivity of adsorption on GTCB to the geometry of molecules and the higher efficiency of capillary columns packed with GTCB in comparison with the usual packed columns, separations of mixtures of two and three families of isomers were carried out.

EXPERIMENTAL

A Chrom-5 analytical gas chromatograph equipped with a flame-ionization detector and rearranged in the laboratory for physico-chemical studies with capillary columns, and also a Varian 3700 gas chromatograph with a MAT 112S mass spectrometer as a specific detector, were used. Three capillary columns were prepared; two of them, 2.2 m × 1 mm I.D. and 4 m × 0.8 mm I.D., were packed with GTCB, and the other was a wall-coated open-tubular (WCOT) capillary column, 30 m × 0.26 mm I.D., containing non-polar SE-30 (Supelco). The method of column packing was described earlier[1,10]. Sterling MT 3100 D4 GTCB with a specific surface area of 7.6 m^2/g was used as the adsorbent. For filling the columns the 0.16–0.18 mm fraction and for the wider capillary the 0.22 0.25 mm fraction were used. Hydrogen was used as the carrier gas for the Chrom-5 and helium for the Varian-MAT instruments. The gases were additionally purified, The optimum gas flow-rate was taken from the relationship between the height equivalent to a theoretical plate (H) and the linear velocity of the carrier gas. The separation of the isomer mixtures was carried out under isothermal conditions at 250 and 270°C on the GTCB capillary column and at 150°C on the SE-30 WCOT column.

The mixtures of high-boiling tricyclic saturated hydrocarbons shown in the formulae were obtained by equilibrium configuration isomerization in a microreactor (40-50 atm of hydrogen, at 500°K, with Group VIII metals as catalyst[5,11]). The

mixture of isomers was dissolved in hexane in the ratio 1:100. Samples of vapour were introduced into the column with a 10-μl syringe without stream splitting.

The columns were connected with the ion source of the mass spectrometer using an open coupling system. The mass chromatograms were obtained at a low electron energy in the range 16–20 eV and also at 70 eV. The emission currents were 0.1 and 0.7 mA, respectively, and temperature of the ionization chamber was 250°C. The total ion current was registered with an integrator in the mass range 455200. Details of the mass spectrometric investigations were reported earlier[12].

RESULTS AND DISCUSSION

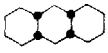
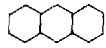
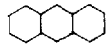
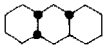
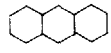
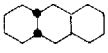
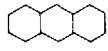
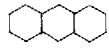
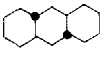
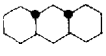
The efficiency of the 4-m GTCB capillary column using a flame-ionization detector and hydrogen as the carrier gas at 250°C was 22,000 theoretical plates with *n*-decane, and that of the 2.2-m GTCB capillary column using a mass spectrometric detector and helium as the carrier-gas at the same temperature was only 4700 theoretical plates. For a similar column 2 m long using a flame-ionization detector with hydrogen as the carrier gas under the same conditions, the efficiency was 19,000 theoretical plates with $H = 0.1$ mm. The lower efficiency with helium as the carrier gas is connected with the higher viscosity of helium and also the broadening of peaks on the way from the capillary column to the ion source of the mass spectrometer. It is notable that the efficiencies of the 2,2-m capillary column and the 30-m WCOT SE-30 column with helium as the carrier gas measured at the optimum temperatures (250 and 150°C) using the first peak on the chromatograms of mixtures of isomers perhydroanthracene and perhydrophenanthrene are close and have $H = 1$ mm.

In Table I, the five isomers of perhydroanthracene and the six isomers of perhydrophenanthrene are arranged in order of increasing retention indices on GTCB. For comparison, the retention indices on SE-30 are also given. The hydrogen atoms projecting above the molecules are indicated with black points in the schematic representation of the molecules. Table I shows that the interval between the retention indices of all isomers of perhydroanthracene and perhydrophenanthrene on GTCB (211 units) exceeds that on SE-30 (89 units). The minimum difference in retention indices of two neighbouring components on the chromatogram of this mixture, containing these two families of isomers, on GTCB is not less then 8 units. This allowed the complete separation of the mixture of all isomers of perhydroanthracene and perhydrophenanthrene on the 2.2-m GTCB capillary column.

Fig. 1 shows the chromatogram of a mixture of these two families of isomers. The numbering of the peaks corresponds to the numbering in Table I. For a qualitative description of the retention of each isomer on GTCB, the ratio of the sums of the distances of all atoms in each isomer for the most advantageous locations of its molecule on the plane, Σr_i, to the sums of these distances for the flattest isomer, Σr_i^*, was used. These distances were evaluated with the help of crude structural models of the isomeric molecules as in a previous paper' (in the molecular-statistical calculations of Henry constants, all possible situations of the molecule were taken into consideration[7,9]). Even a small difference in the geometry of the isomers was sufficient for their complete separation on a uniform flat surface of GTCB. Such a sensitivity of adsorption on GTCB to the differences in the geometry of molecules is based on the one-sided influence of the intermolecular force field of the adsorption

TABLE 1

KOVÁTS RETENTION INDICES (I) OF ISOMERS OF PERHYDROANTHRACENE AND PERHYDROPHENANTHRENE

Peak No.	*Structure*	*GTCB capillary column*		*SE-30 WCOT column*	
		Isomer	$I^{GTCB}_{250°C}$	*Structure*	$I^{SE\text{-}30}_{150°C}$
1		*cis–syn–cis*	*1125*		*1479*
2		*cis–syn–cis*	*11.56*		*1491*
3		*cis–anti trans*	*1179*		*1493*
4		*cis–anti cis*	*1196*		*1512*
5		*cis–syn–trans*	*1207*		*1512*
6		*cis–anti–cis*	*1241*		1535
7		*trans–syn cis*	*1263*		*1546*
8		*trans syn trans*	*1290*		*1547*
9		*trans anti trans*	*1302*		1561
10		*trans-anti trans*	*1310*		1562
11		*trans syn trans*	1336		1568
			ΔI = 211		*ΔI = 89*

of the force centres of the molecule and on the additivity of the energies of interaction of the molecules with GTCB on these force centres[9]. By calculating the sums of distances, it was taken into account that the molecules on the surface are situated in the energetically most advantageous position, e.g., at a potential minimum. In gas–liquid chromatography the molecules of the stationary phase surround the molecules of the isomers on all sides, and therefore geometric differences in the molecular structure do not influence the differences in intermolecular interactions so much as in adsorption on the flat surface of GTCB. It can be seen from Table I that of eleven

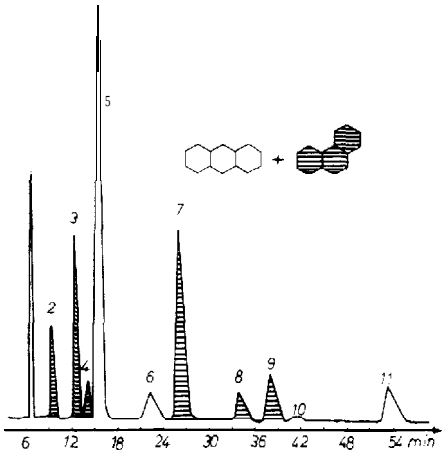


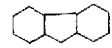
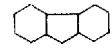
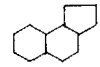
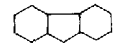
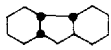
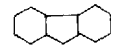
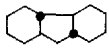
Fig. 1. Separation of a mixture of tricyclotetradecane stereoisomers (five isomers of perhydroanthracene and six isomers of perhydrophenanthrene) on a GTCB capillary column (2.2 m × 1 mm I.D.). Particle size, 0.22–0.25 mm; column temperature, 250°C: helium flow-rate, 10 ml/min; pressure drop, 5.2 atm; flame-ionization detector. The numbers on the peaks correspond to the numbers in Table I.

components of the mixture, eight of them on SE-30 have retention indices almost identical with that of the neighbouring component. It is evident that this mixture cannot be completely separated on the SE-30 WCOT column (for separation on this stationary phase it would be necessary to increase the efficiency of the column by at least a factor of 10). The sequence of emergence of the isomers in gas-adsorption (on GTCB) and in gas--liquid (on SE-30) chromatography do not coincide; in the former instance the isomer molecules that have fewer contacts with the GTCB surface elute first because they are the most bent molecules, and the flattest molecules elute last.

In the same way, the separation of another mixture of fourteen isomers of three families of tricyclotridecane containing five isomers of perhydrofluorene, seven isomers of 1,2-cyclopentanodecalin and two isomers of perhydrophenalene was carried out. As in the previous instance, every family of isomers has a different order of junction of rings (see formulae). The retention indices of the isomers of these compounds obtained on the GTCB capillary column and, for comparison, on the SE-30 WCOT column are given in Table II in order of their grow on GTCB. It can be seen that the interval of retention indices of the isomers of these families on GTCB is much higher than that on SE-30 (234 and 89 units, respectively). On the SE-30 WCOT column even the isomers of one family, such as perhydrofluorene or 1,2-cyclopentanodecalin, could not be separated. On the chromatogram of perhydrofluorene obtained on an SE-30 gas liquid chromatographic column[3,4,6] only four peaks were found compared with five on GTCB, and on that of 1,2-cyclopentanodecalins only six peaks were found compared with seven peaks on GTCB. Hence it cannot be expected that the mixture of all three families could be completely separated on the SE-30 column. In the separation of individual families on GTCB the minimum difference between the neighbouring components was 5 retention index units. If the efficiency of the GTCB capillary column is double that of the columns used earlier[4], it makes it possible to separate all fourteen components of the isomers of the three

TABLE II

KOVÁTS RETENTION INDICES OF ISOMERS OF 1,2-CYCLOPENTANODECALIN, PERHYDROFLUORENE AND PERHYDROPHENALENE

Peak No.	*Structure*	*GTCB capillary column*		SE-30 *WCOT column*	
		Isomer	$I^{GTCB}_{250°C}$	*Structure*	$I^{SE-30}_{150°C}$
1		*cis-syn cis*	1041		1370
2		*cis anti cis*	1078		1375
3		*cis-syn-cis*	1094		1385
4		*trans syn cis*	1107		1393
5		*cis-syn trans*	1120		1411
6		*cis anri cis*	1125		1420
7		*cis-anti trans*	1141		1422
8		*cis-syn trans*	1150		1428
9		*cis anti trans*	1169		1431
10		*trans anti cis*	1212		1437
11		*trans anti-trans*	1231		1443
12		*cis-trans cis*	1248		1459
13		*trans trans trans*	1266	—	–
14		*trans anti-trans*	1275	—	–
			AI = 234		*AI* = 89

families of investigated tricyclotridecanes. Fig. 2 shows the chromatogram of this mixture of isomers, which can be formed by catalytic hydrogenation of fluorene. The chromatogram was obtained on a GTCB capillary column (4 m × 0.8 mm I.D.) with

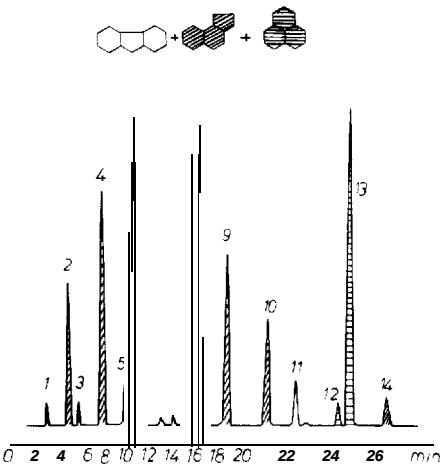


Fig. 2. Separation of a mixture of tricyclotridecane stereoisomers (seven isomers of 1,2-cyclopentanodecalin, five isomers of perhydrofluorene and two isomers of perhydrophenalene) on a GTCB capillary column, Column temperature, 270°C; hydrogen flow-rate, 8 ml/min; pressure drop, 5.4 atm; flame-ionization detector. The numbers on the peaks correspond to the numbers in Table II.

a flame-ionization detector. The peak numbers in Fig. 2 correspond to the numbers of the components in Table II.

The complete separation of the investigated substances in this work indicates that it may be possible to use GTCB capillary columns in the analysis of mixtures of isomers obtained by catalytic hydrogenation, and to use mass spectrometry of the individual isomers in order to identify the dependence of the fragmentation of the molecules on their structure[12]. This is of interest for the comparison of the strains in molecules of different isomers of polycyclic systems and for chromatoscopic investigations of the structures of isomer molecules.

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