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CHARACTERIZATION OF MONOALKYLCYCLOPENTADIENS BY RETENTION-STRUCTURE CORRELATION IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The retention behaviour of 32 synthesized C_6–C_{15} monoalkylcyclopentadienes was studied by capillary gas chromatography on squalane and Carbowax 20M stationary phases. Alkylcyclopentadienes were characterized on the basis of retention–structure relationships. An equation describing precisely the retention behaviour of the first six members of homologous series of alkylcyclopentadiens and that permits the determination of the contribution of stereochemical and conformational properties (propyl effect) of the structure of homologues to their retention is presented. The propyl effect is valid for monoalkylcyclopentadiens in which the propyl group is situated on a carbon atom bearing both double and single bonds in the cyclopentadiene ring.

INTRODUCTION

With the aim of characterizing hydrocarbons by capillary gas chromatography, we have studied monoalkylcyclopentadienes in detail. The compounds originate from the thermal treatment (pyrolysis, hydrocracking) of crude oil fractions and represent interesting petrochemical raw materials. Cyclopentadienes have so far been less well studied gas chromatographically than other types of hydrocarbons. Retention indices have been published only for 1,3-cyclopentadiene[1–4], 1-methyl-1,3-cyclopentadiene and 2-methyl-1,3-cyclopentadiene[4] on squalane and for 5-methyl-1,3-cyclopentadiene[5] on SE-30 as the stationary phase. The retention behaviour of higher alkylhomologues of 1,3-cyclopentadiene has not previously been studied.

The aim of this work was to study the gas chromatographic retention behaviour of C_6–C_{15} monoalkylcyclopentadienes. For this purpose, mixtures of isomers of alkyl-1,3-cyclopentadienes were synthesized, their retention indices were measured on non-polar and polar stationary phases and they were characterized on the basis of retention–structure relationships.

EXPERIMENTAL

Thirty-two monoalkyl-substituted C_6–C_{15} 1,3-cyclopentadienes were obtained by alkylation of 1,3-cyclopentadiene with alkyl iodides or alkyl bromides in the presence of sodium metal dissolved in liquid ammonia[6,7]. By this means isomeric mixtures especially of 1- and 2-alkyl derivatives with smaller amounts of 5-alkyl derivatives of 1,3-cyclopentadiene were prepared. The initial 1,3-cyclopentadiene was prepared by thermal decomposition of dicyclopentadiene followed by rectification and its purity was 99%.

The retention characteristics of model mixtures of alkylcyclopentadienes were measured on a Perkin-Elmer F17 gas chromatograph with a flame ionization detector. They were separated in capillary columns (50 m × 0.25 mm I.D.) coated with either squalane or Carbowax 20M, with a stationary phase film thickness of 0.25 μm; hydrogen was used as the carrier gas and the efficiency of the columns was 120 000 theoretical plates. The standard deviation of measurements of retention indices was 0.06 index unit (i.u.) on squalane and 0.09 i.u. on Carbowax 20M.

RESULTS AND DISCUSSION

Measured retention indices of alkylcyclopentadienes on squalane and Carbowax 20M, their homomorphous factors (H), temperature coefficients of the retention indices (dI/dT) and differences in retention indices on Carbowax 20M and squalane (ΔI) are given in Table I.

For identification of methylcyclopentadienes the published retention indices and for other alkylcyclopentadienes the correlations between molecular structure and retention behaviour were used.

The separation systems used were characterized by comparison of the measured and published retention indices of alkylcyclopentadienes. The published retention indices for 1,3-cyclopentadiene on squalane at 27°C, *i.e.*, 514.9[1], 516.6[2], 518.1[3] and 518.6[4], show a relatively wide range of 3.7 i.u.; the measured value at 27°C was 516.0. For methyl-1,3-cyclopentadienes on squalane, the published retention indices[4] are, including 1,3-cyclopentadiene, on average 2.2 i.u. higher than the measured values given in Table I. This agrees with the previous conclusion[8] that the retention indices of unsaturated hydrocarbons in the literature[4] are generally higher, proportional to their polarity, for aromatic hydrocarbons by as much as 4 i.u. Comparison of the retention index of benzene measured in the squalane column with high-precision measurements by Rijks and Cramers[9] showed a difference of 0.2 i.u. This shows the close similarity of the two separation systems and also comparability of retention indices of hydrocarbons measured with them.

The reproducibility of measurements of the retention indices of alkylcyclopentadienes on Carbowax 20M is also influenced by adsorption of hydrocarbons on the interphase between the carrier gas and the polar stationary phase, depending on the surface area–volume ratio of the stationary phase, or on the thickness of the sta-

TABLE I

RETENTION INDICES, HOMOMORPHOUS FACTORS, TEMPERATURE COEFFICIENTS OF RETENTION INDICES AND ΔI VALUES OF ALKYLCYCLOPENTADIENES

Cyclopentadiene	I_{64}^{SQ}	H_{64}^{SQ}	$10\,(dI^{SQ}/dT)$	I_{64}^{CW}	ΔI_{64}^{CW-SQ}
1,3-Cyclopentadiene	523.1	23.1	1.92	745.7	222.6
2-Methyl-1,3-cyclopentadiene	624.4	24.4	1.33	834.2	209.8
1-Methyl-1,3-cyclopentadiene	626.2	26.2	0.92	844.5	218.3
5-Methyl-1,3-cyclopentadiene	645.9	45.9	1.17	870.4	224.5
2-Ethyl-1,3-cyclopentadiene	723.8	23.8	0.75	930.3	206.5
1-Ethyl-1,3-cyclopentadiene	727.6	27.6	0.75	940.4	212.8
5-Ethyl-1,3-cyclopentadiene	747.6	47.6	0.92	966.7	219.1
2-Isopropyl-1,3-cyclopentadiene	785.4	−14.6	1.66		
1-Isopropyl-1,3-cyclopentadiene	787.8	−12.2	1.66		
2-*n*-Propyl-1,3-cyclopentadiene	812.6	12.6	0.83	1010.0	197.4
1-*n*-Propyl-1,3-cyclopentadiene	816.4	16.4	0.75	1020.2	203.8
5-*n*-Propyl-1,3-cyclopentadiene	835.1	35.1	0.75	1046.6	211.5
2-Isobutyl-1,3-cyclopentadiene	864.1	−35.9	1.83	1043.6	179.5
1-Isobutyl-1,3-cyclopentadiene	867.0	−33.0	1.83	1052.1	185.1
2-*n*-Butyl-1,3-cyclopentadiene	912.6	12.6	0.92	1108.2	195.6
1-*n*-Butyl-1,3-cyclopentadiene	916.5	16.5	1.08	1118.1	201.6
5-*n*-Butyl-1,3-cyclopentadiene	933.9	33.9	1.08	1144.5	210.6
exo-Dicyclopentadiene	986.2	86.2			
endo-Dicyclopentadiene	989.1	89.1	3.25	1245.1	252.4
2-*n*-Pentyl-1,3-cyclopentadiene	1007.9	7.9	1.33	1205.0	197.1
1-*n*-Pentyl-1,3-cyclopentadiene	1011.8	11.8	1.33	1215.0	203.2
5-*n*-Pentyl-1,3-cyclopentadiene	1028.8	28.8	1.33		
2-*n*-Hexyl-1,3-cyclopentadiene	1107.1	7.1	1.42	1302.0	194.9
1-*n*-Hexyl-1,3-cyclopentadiene	1111.1	11.1	1.42	1311.8	200.7
5-*n*-Hexyl-1,3-cyclopentadiene	1128.4	28.4	1.42	1339.1	210.7
2-*n*-Heptyl-1,3-cyclopentadiene	1206.4	6.4	1.58	1399.4	193.0
1-*n*-Heptyl-1,3-cyclopentadiene	1210.5	10.5	1.58	1409.5	199.0
5-*n*-Heptyl-1,3-cyclopentadiene	1227.8	27.8	1.58		
2-*n*-Octyl-1,3-cyclopentadiene	1306.1	6.1		1497.1	191.0
1-*n*-Octyl-1,3-cyclopentadiene	1309.9	9.9		1507.3	197.4
5-*n*-Octyl-1,3-cyclopentadiene	1327.6	27.6			
2-*n*-Nonyl-1,3-cyclopentadiene	1406.6	6.0			
1-*n*-Nonyl-1,3-cyclopentadiene	1409.7	9.7			
2-*n*-Decyl-1,3-cyclopentadiene	1505.9	5.9			
1-*n*-Decyl-1,3-cyclopentadiene	1509.6	9.6			

tionary phase film. For cyclopentadienes, comparative retention indices on Carbowax 20M are not available. Comparison at monoalkylcyclohexadienes, for which retention indices on Carbowax 20M have been published[10], showed that the retention indices measured with the separation system used were on average 10 i.u. higher.

The investigation of molecular structure–retention behaviour relationships as a suitable means of characterizing hydrocarbons is based on the fact that, on the one hand, the samples contain a large number of possible hydrocarbon components and, on the other, there is lack of reference materials and published retention data, or they are not sufficiently reproducible, and certain limitations exist as to identification of isomers by a combination of chromatographic and spectral methods. The system of correlations used here is based on the homology of hydrocarbons. It is assumed that, for the first members of the homologous series, the dependence of retention characteristics on the number of carbon atoms is not linear and there is a possibility of the manifestation of the stereochemical and conformational properties of homologues[11].

The homomorphous factor, defined as the difference between the retention indices of the sample substance and an *n*-alkane with the same number of carbon atoms (H) or with an analogous carbon skeleton[2] characterizes the contribution of the functional group to the retention index of the sample substance. From the graph of the homomorphous factor of the studied dienes on squalane *versus* carbon number (Fig. 1), it is evident that H for homologous series (except the first member) decreases asymptotically with increasing number of carbon atoms, and from the seventh member they become nearly constant. This dependence permits the calculation of the retention indices of homologues having more than six carbons in their alkyl chain with an accuracy of tenths of an index unit. A similar dependence was also observed for homologous series of other hydrocarbons[11].

Systematic deviations from the regularity of the dependence $H^{SQ} = f(C_n)$ in the direction of lower retention values for 1-, 2- and 5-*n*-propyl-substituted deriva-

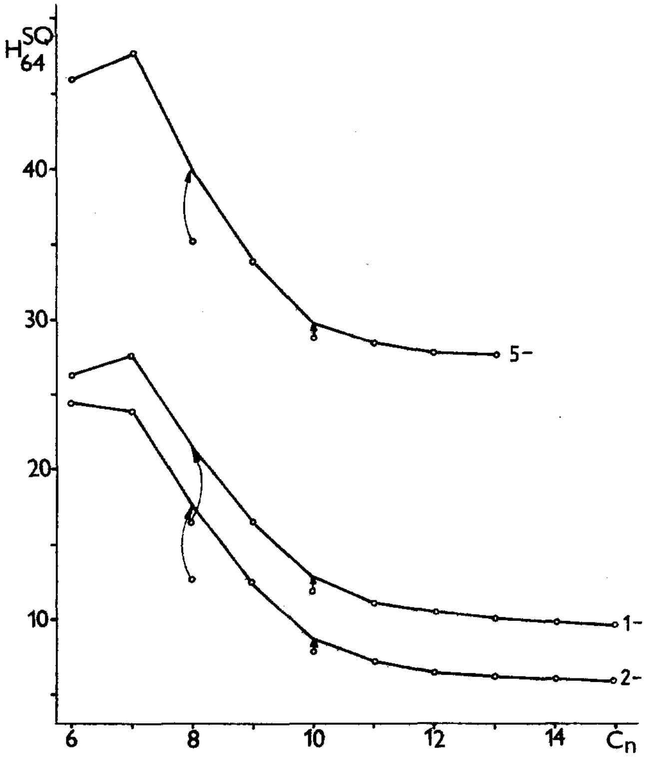
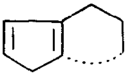


Fig. 1. Dependence of the homomorphous factor, H, on the number of carbon atoms for homologous series of alkyl-1,3-cyclopentadienes on squalane at 64°C. 1- = 1-Alkyl-; 2- = 2-alkyl-; 5- = 5-alkyl-1,3-cyclopentadienes. The arrows indicate the anomalous behaviour of propyl and pentyl derivatives.

tives of 1,3-cyclopentadiene again demonstrate the influence of the propyl effect, *i.e.*, an intramolecular interaction between the propyl group and the π-electron system of the molecule[12]. The form of the propyl group permits the cyclic conformation



to be formed, as a consequence of which such homologues have lower retention characteristics than those following from the regularity of the dependence $H = f(C_n)$ for homologous series of alkylcyclopentadienes. This corresponds to the fact[13] that in comparison with straight-chain conformations the so-called squeezed conformations, which form structures with a possible propyl effect, have lower physico-chemical properties such as density, refractive index and melting point, weaker Van der Waals interactions, etc.

An equation for the retention behaviour of members of homologous series was presented by Golovnya and Grigoryeva[14]. This equation, modified so that the denominator of the fourth term was considered as a reciprocal, was used to calculate the contribution of the propyl effect to the retention index of anomalous *n*-propylcyclopentadienes:

$$I = a + bm + c \cdot \frac{\log m}{m} + \frac{d}{1/[(m-2)^2 + 0.1]}$$

where I is the retention index, m is the serial number of the homologue in the homologous series and a, b, c and d are coefficients dependent on the conditions of the gas chromatographic analysis and on the character of the functional groups of homologous series.

The coefficients of the equation were calculated from retention indices of the first, second, fourth and sixth members of the studied homologous series of alkylcyclopentadienes on both squalane and Carbowax 20M and their values are given in Table II. As can be seen from Tables III and IV, the calculated retention indices for homologues with the serial numbers $m = 1$–6, except the third and fifth members (propyl and pentylderivatives of cyclopentadienes), are almost identical with the measured values, the greatest deviation being 0.1 i.u. For higher homologues ($m > 6$), the difference between the calculated and measured retention indices, δI, increases

TABLE II

COEFFICIENTS a, b, c AND d OF THE EQUATION FOR RETENTION OF ALKYL-1,3-CYCLOPENTADIENES ON SQUALANE AND CARBOWAX 20M AT 64°C

Cyclopentadiene	*Squalane*				*Carbowax 20M*			
	a	*b*	*c*	*d*	*a*	*b*	*c*	*d*
2-Alkyl-	530.76	92.71	50.01	0.84	747.25	84.50	91.87	2.23
1-Alkyl-	532.54	92.69	63.68	0.88	757.66	84.38	91.43	2.24
5-Alkyl-	553.86	90.68	81.46	1.24	783.61	84.20	95.99	2.35

TABLE III

MEASURED AND CALCULATED RETENTION INDICES OF ALKYL-1,3-CYCLOPENTADIENES ON SQUALANE AT 64°C AND THEIR DIFFERENCES, δI

Alkyl	*2-Alkyl-*			*1-Alkyl-*			*5-Alkyl*		
	I_{64}^{SQ} *(meas.)*	I_{64}^{SQ} *(calc.)*	δI	I_{64}^{SQ} *(meas.)*	I_{64}^{SQ} *(calc.)*	δI	I_{64}^{SQ} *(meas.)*	I_{64}^{SQ} *(calc.)*	δI
Methyl	624.4	624.4	0.0	626.2	626.2	0.0	645.9	645.9	0.0
Ethyl	723.8	723.8	0.0	727.6	727.6	0.0	747.6	747.6	0.0
n-Propyl	812.6	817.8	−5.2	816.4	821.7	−5.3	835.1	840.2	−5.1
n-Butyl	912.6	912.6	0.0	916.5	916.5	0.0	933.9	933.9	0.0
n-Pentyl	1007.9	1008.9	−1.0	1011.8	1012.9	−1.1	1028.8	1029.9	−1.1
n-Hexyl	1107.1	1107.0	0.1	1111.1	1111.1	0.0	1128.4	1128.5	−0.1
n-Heptyl	1206.4	1206.9	−0.5	1210.5	1211.2	−0.7	1227.8	1229.6	−1.8
n-Octyl	1306.1	1308.4	−2.3	1309.9	1313.0	−3.1	1327.6	1333.3	−5.7

and therefore to describe the retention behaviour of the higher members of the homologous series, the original equation[14] is more precise.

The calculated contribution of the propyl effect to the retention indices of anomalous 1-, 2- and 5-*n*-propyl-1,3-cyclopentadienes on squalane is between −5.1 and −5.3 i.u. It is almost the same for the propyl group bound to a carbon atom with double or single bonds, which is connected with delocalization of the electron cloud over all the carbon atoms of the cyclopentadiene ring. In contrast, with alkylcyclopentenes, the propyl effect appeared only for structures having the propyl group bound to a carbon atom with a double bond, *i.e.*, for 1-propylcyclopentene but not 3-propylcyclopentene[12] (Table V). The calculated contribution of the propyl effect for 1-propyl-1-cyclopentene of −4.7 i.u. is close to the value of −5.0 i.u. obtained by graphical interpolation of the dependence $H = f(C_n)$ for the homologous series of 1-alkyl-1-cyclopentenes[12].

The dependence of the homomorphous factors, $\bar{H}$, obtained by subtracting

TABLE IV

MEASURED AND CALCULATED RETENTION INDICES OF ALKYL-1,3-CYCLOPENTADIENES ON CARBOWAX 20M AT 64°C AND THEIR DIFFERENCES, δI

Alkyl	*2-Alkyl-*			*1-Alkyl-*			*5-Alkyl*		
	I_{64}^{CW} *(meas.)*	I_{64}^{CW} *(calc.)*	δI	I_{64}^{CW} *(meas.)*	I_{64}^{CW} *(calc.)*	δI	I_{64}^{CW} *(meas.)*	I_{64}^{CW} *(calc.)*	δI
Methyl	834.2	834.2	0.0	844.5	844.5	0.0	870.4	870.4	0.0
Ethyl	930.3	930.3	0.0	940.4	940.4	0.0	966.7	966.7	0.0
n-Propyl	1009.9	1017.8	−7.9	1020.2	1027.8	−7.6	1046.6	1054.1	−7.5
n-Butyl	1108.2	1108.2	0.0	1118.1	1118.1	0.0	1144.5	1144.5	0.0
n-Pentyl	1205.0	1202.9	2.1	1215.0	1212.7	2.3	1242.0	1239.4	2.6
n-Hexyl	1302.0	1302.1	−0.1	1311.8	1311.9	−0.1	1339.1	1339.1	0.0
n-Heptyl	1399.4	1405.9	−6.5	1409.5	1415.6	−6.1	1436.6	1443.6	−7.0

TABLE V

MEASURED AND CALCULATED RETENTION INDICES OF ALKYLCYCLOPENTENES ON SQUALANE AT 64°C AND THEIR DIFFERENCES, δI

Alkyl	*1-Alkyl-1-cyclopentene*			*3-Alkyl-1-cyclopentene*		
	I^{SQ}_{64} *(meas.)*	I^{SQ}_{64} *(calc.)*	δI	I^{SQ}_{64} *(meas.)*	I^{SQ}_{64} *(calc.)*	δI
Methyl	646.4	646.4	0.0	605.2	605.2	0.0
Ethyl	748.2	748.2	0.0	714.8	714.8	0.0
n-Propyl	836.3	841.0	−4.7	813.0	813.2	−0.2
n-Butyl	934.8	934.8	0.0	911.1	911.1	0.0
n-Pentyl	1032.1	1030.9	1.2	1009.7	1009.7	0.0
n-Hexyl	1129.3	1129.4	−0.1	1109.4	1109.4	0.0
n-Heptyl	1228.6	1230.4	−1.8	1209.2	1210.0	−0.8
n-Octyl	1328.4	1333.8	−5.4	1309.1	1311.7	−2.6

from the retention index of alkylcyclopentadienes the retention index of alkylcyclopentanes with the same carbon skeleton, on the number of carbon atoms for homologous series of alkyl-1,3-cyclopentadienes on squalane is illustrated in Fig. 2, where the influence of the propyl effect can also be seen.

It can be seen from Table IV that the contribution of the propyl effect to the retention index of propylcyclopentadienes is higher on polar Carbowax 20M than on non-polar squalane; it is between −7.5 and −7.9 i.u., which is due to the steric hindrance effect of the twisted propyl group on the solute–solvent interaction[12].

The data in Tables III and IV (and also in Figs. 1 and 2) also show certain deviations (on average four times smaller than in the case of the propyl effect) in the retentions of *n*-pentyl derivatives of 1,3-cyclopentadiene from the values following from the regularity of retention in homologous series. It follows from the data in Table V that such a pentyl effect occurs only for homologous series with a propyl effect. The deviations, however, are not systematic: for pentylcyclopentadienes on squalane they are negative and on Carbowax 20M positive, and for 1-pentyl-1-cyclopentene on squalane also positive. The reason may be the zig-zag arrangement of the carbon chain (structures with the chain prolonged in the direction of the molecular axis are characterized by an increased retention).

Individual isomers of alkylcyclopentadienes eluate in the order 2- < 1- < 5-alkyl-1,3-cyclopentadiene. In comparison with squalane, the difference in retention between 2- and 1-alkyl isomers increased for methyl derivatives from 2 to 10 i.u. and for other alkyl derivatives from 4 to 10 i.u. on Carbowax 20M. In contrast to aliphatic conjugated dienes, for which an increase in retention indices on squalane of 30–60 i.u. in comparison with the corresponding alkenes is typical, for alkylcyclopentadienes the retention indices for 1-alkyl-1,3-cyclopentadienes are lower than those of 1-alkyl-1-cyclopentenes by 18–20 i.u. This is probably due to delocalization of π-electrons of the 1,3-cyclopentadiene molecule in comparison with cyclopentene. The branched alkyl substituents show lower retentions than the corresponding unbranched alkylsubstituents of 1,3-cyclopentadienes, *e.g.*, at butylcyclopentadienes on squalane by 49 and on Carbowax 20M by 65 i.u.

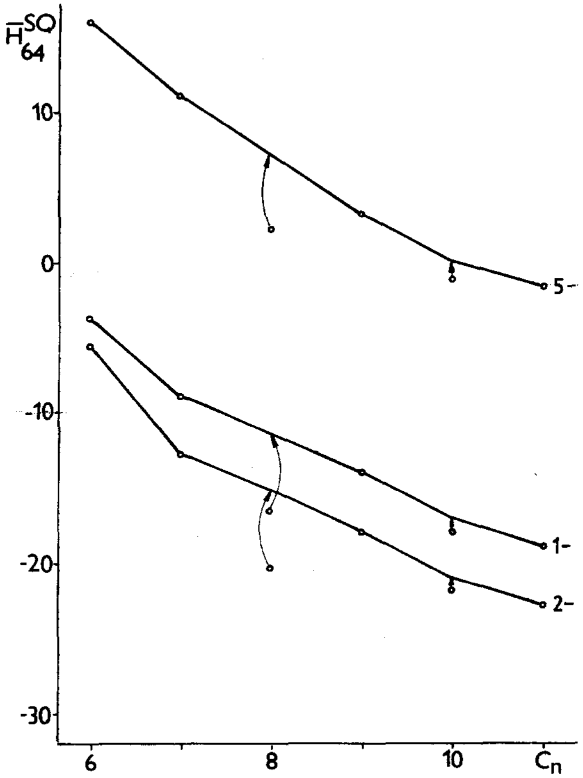


Fig. 2. Dependence of the homomorphous factor, $\bar{H}$, on the number of carbon atoms for homologous series of alkyl-1,3-cyclopentadienes on squalane at 64°C. 1- = 1-Alkyl-; 2- = 2-alkyl-; 5- = 5-alkyl-1,3-cyclopentadienes.

The temperature coefficients of the retention indices of alkylcyclopentadienes on squalane, 10(d*I*/d*T*), (Table I) were calculated from retention indices measured at 52 and 64°C. They are between 0.75 and 1.83 and are substantially higher for branched alkylcyclopentadienes than for the corresponding unbranched compounds. In homologous series, the values of d*I*/d*T* decrease for the second or third member and then increase, while the differences between isomers decrease and for homologues with more than five carbon atoms in the alkyl chain the d*I*/d*T* values for isomers are almost identical.

The difference in the retention indices of alkylcyclopentadienes on Carbowax 20M and on squalane, ΔI, as a function of the location of the alkyl group in the molecule, increase in the order 2- < 1- < 5-alkyl-1,3-cyclopentadiene, *i.e.*, in the same order in which the retentions of isomers increase.

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