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DI-*n*-BUTYL TETRACHLOROPHTHALATE AS A LIQUID PHASE IN THE GAS CHROMATOGRAPHIC IDENTIFICATION OF HYDROCARBONS

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SUMMARY

Retention indices of 78 hydrocarbons (including branched alkanes, branched alkenes, cycloalkanes, alkylbenzenes and some bicyclic compounds) have been determined on di-*n*-butyl tetrachlorophthalate over the range 50–120° using open tubular columns, and are compared with the corresponding data on squalane. The temperature variation of the retention index on the tetrachlorophthalate can be correlated with molecular structure, and displays certain features which are absent from other stationary phases. In particular, alkylbenzenes can be distinguished from alkylcyclohexanes, and a sub-classification of alkylbenzenes according to the number of substituents appears to be possible on the basis of the temperature increments.

INTRODUCTION

The Kováts retention index is a powerful aid to qualitative analysis by gas chromatography (GC) and the collection of sets of retention index data in the literature contributes to the identification of individual components in complex mixtures. The validity of the identification can be greatly enhanced by using stationary phases of different polarity and/or different working temperatures. In many cases, the latter possibility has certain advantages over the former, since on different columns the elution order can be altered and it may be difficult to recognize the corresponding peaks. The temperature variation of the retention index, on the other hand, has been shown by many workers¹⁻⁹ to be a valuable additional criterion which reflects certain structural features of the compounds chromatographed.

The present paper reports retention indices for 78 hydrocarbons of various types measured over a wide temperature range (50–120°) on di-*n*-butyl tetrachlorophthalate (BTCF) stationary phase. The tetrahalogenophthalate esters are known for their weak complexing (electron-acceptor) character and their unique selectivity in the separation of aromatics^{10,11}, especially for reversing the usual elution order of *meta*- and *para*-isomers; more recently, their usefulness has been demonstrated¹² for the separation of geometric and positional *n*-olefin isomers. Retention data reported in the literature for the separation of hydrocarbons on these esters include the relative

retentions of paraffins, olefins and aromatics on methyl propyl and di-*n*-butyl tetrachlorophthalates¹⁰, on di-*n*-propyl tetrachlorophthalate^{10,13} and on di-*n*-propyl tetrabromophthalate¹⁰, specific retention volumes of some higher aromatic compounds on di-*n*-nonyl tetrachlorophthalate¹¹, relative retentions of all of the C₆-C₁₀ alkylbenzenes on di-*n*-propyl tetrachlorophthalate¹⁴ and retention indices of all of the C₇-C₁₀ *n*-alkenes on di-*n*-butyl and bis(2-ethylhexyl) tetrachlorophthalates¹².

EXPERIMENTAL

The measurements were made on a Chrom 4 gas chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia) equipped with a flame-ionization detector; the carrier gas was nitrogen. Two wall-coated open tubular stainless-steel columns were used, both of the same dimensions (50 m × 0.25 mm I.D.) and prepared by the same technique but differing in the amount of stationary phase deposited. Column A had a capacity ratio $k = 2.6$ for *n*-nonane (measured at 60°) and was used mainly for the measurements at lower temperatures and with compounds of higher boiling points, whereas column B had a capacity factor $k = 6.9$ and was used for compounds of lower boiling points and at higher temperatures. The BTCP substrate was purchased from May & Baker, Dagenham, Great Britain, and the open tubular columns were coated by the standard dynamic procedure using a 10% (w/w) solution of BTCP in chloroform. The chromatographic efficiencies, based on *n*-nonane at 60° and an inlet pressure of 2.1 bar, were $n = 110,000$ theoretical plates for column A and $n = 72,000$ theoretical plates for column B.

The branched olefins investigated in this study were prepared by procedures described elsewhere^{15,16}. The octalins and the tri- and tetra-substituted benzenes were kindly supplied by Dr. J. Závada of this Institute. The other hydrocarbon samples were commercial products, obtained from various sources (Lachema, Brno, Czechoslovakia; Fluka, Buchs, Switzerland; Aldrich, Milwaukee, Wisc., U.S.A.). The experiments were conducted with suitably prepared mixtures containing *n*-alkane standards. The first three (C₅, C₆, C₇) *n*-alkanes were used for the determination of the gas hold-up time of the capillaries (according to the method developed by Peterson and Hirsch¹⁷), whereas adjacent *n*-alkanes that bracketed the compounds of interest were used in determining the relevant index data. Overlapping of peaks was avoided; when co-elution of a particular compound with a *n*-alkane standard occurred, this *n*-alkane was omitted from the mixture and a secondary standard having a predetermined retention index was used instead.

Injections were made by means of a 0.5- μ l SGE microsyringe and a splitting ratio of 1:500 was generally maintained. The amount injected onto the column was within the linear dynamic range (*cf.* ref. 18) at *ca.* 0.02 μ g per component. The retention indices given are mean values from at least six individual determinations; the standard deviation lay between ± 0.15 and ± 0.33 . A check of the mutual agreement between the two columns A and B revealed that identical results were obtained for all of the hydrocarbons with the exception of alkylbenzenes, indane and tetralin. For these aromatics, a systematic deviation was found, with higher indices on column A, the difference being constant at 0.8–0.9 irrespective of temperature. This deviation is ascribed to a slight difference in the primary adsorptivity of the capillary walls. In the

TABLE I

RETENTION INDICES OF BRANCHED ALKANES ON DI-*n*-BUTYL TETRACHLORO-PHTHALATE AT 50 AND 100°, THEIR TEMPERATURE COEFFICIENTS AND COMPARISON WITH DATA ON SQUALANE

Compound	BTCP		SQ		BTCP - SQ
	I_{50}	I_{100}	$10 \cdot \frac{dI}{dT}$	$10 \cdot \frac{dI}{dT}$	ΔI_{100}
2-Methylbutane	475.4	476.2	0.16	0.07	0.6
2-Methylpentane	569.8	570.9	0.22	0.17	0.4
2-Methylhexane	666.3	667.3	0.20	0.17	-0.1
2-Methylheptane	764.3	756.5	0.24	0.15	-0.1
2-Methyloctane	863.6	864.8	0.24	0.15*	-0.4*
3-Methylpentane	588.6	590.6	0.40	0.45	4.2
3-Methylhexane	679.3	681.2	0.38	0.36	3.2
3-Methylheptane	774.3	776.2	0.38	0.31	2.4
3-Methyloctane	871.5	873.3	0.36	0.30	1.6
3-Ethylpentane	691.7	694.9	0.64	0.57	6.1
4-Ethylheptane	859.2	861.7	0.50	0.40*	1.8*
2,2-Dimethylbutane	539.6	544.4	0.96	0.82	3.5
2,2-Dimethylpentane	625.2	628.9	0.74	0.65	0.1
2,2-Dimethylhexane	716.2	719.7	0.70	0.52	-2.3
2,4-Dimethylpentane	629.1	632.4	0.66	0.35	0.9
2,4-Dimethylhexane	732.8	736.2	0.68	0.51	1.8
2,4-Dimethylheptane	818.8	821.3	0.50	0.45*	-1.1*
2,5-Dimethylhexane	727.2	729.3	0.42	0.30	-0.6
2,2,4-Trimethylpentane	692.9	700.4	1.50	1.09	5.1
2,3,5-Trimethylhexane	814.4	820.2	1.16	0.84	4.0

* Data for squalane from ref. 24, otherwise from ref. 19.

TABLE II

RETENTION INDICES OF CYCLOALKANES ON DI-*n*-BUTYL TETRACHLORO-PHTHALATE AT 50 AND 100°, THEIR TEMPERATURE COEFFICIENTS AND COMPARISON WITH DATA ON SQUALANE

Compound	BTCP		SQ		BTCP - SQ
	I_{50}	I_{100}	$10 \cdot \frac{dI}{dT}$	$10 \cdot \frac{dI}{dT}$	ΔI_{100}
Cyclopentane	574.5	584.5	2.00	1.38	11.9
Methylcyclopentane	639.7	649.4	1.94	1.52	13.9
Ethylcyclopentane	749.4	760.4	2.20	1.83	17.4
1,1-Dimethylcyclopentane	685.2	698.2	2.60	1.83	15.6
1- <i>cis</i> -3-Dimethylcyclopentane	694.3	703.4	1.82	1.63	12.6
1- <i>trans</i> -2-Dimethylcyclopentane	707.0	716.0	1.80	1.59	18.9
<i>n</i> -Propylcyclopentane	845.0	855.7	2.14	1.84	16.2
Cyclohexane	672.0	687.1	3.02	2.22	13.3
Methylcyclohexane	743.4	758.8	3.08	2.43	20.8
Ethylcyclohexane	852.3	868.9	3.32	2.69	21.2
<i>n</i> -Propylcyclohexane	943.6	959.9	3.26	2.4*	21.9*
<i>n</i> -Butylcyclohexane	1039.4	1055.4	3.20	2.7*	17.8*
<i>tert.</i> -Butylcyclohexane	996.1	1019.1	4.60	3.7*	21.6*

* Data for squalane from ref. 24, otherwise from ref. 19.

TABLE III

RETENTION INDICES OF BRANCHED ALKENES ON DI-*n*-BUTYL TETRACHLORO-PHTHALATE AT 50 AND 100°, THEIR TEMPERATURE COEFFICIENTS AND COMPARISON WITH DATA ON SQUALANE²⁴

Compound	BTCP		SQ		BTCP - SQ
	I_{50}	I_{100}	$10 \cdot \frac{dI}{dT}$	$10 \cdot \frac{dI}{dT}$	
2-Methyl-2-nonene	1010.0	1009.5	-0.10	0.10	24.2
2-Methyl- <i>trans</i> -3-nonene	948.4	950.6	0.44	0.52	13.4
2-Methyl- <i>cis</i> -3-nonene	946.8	950.3	0.70	0.66	18.8
2-Methyl- <i>trans</i> -4-nonene	959.3	961.2	0.38	0.46	15.6
2-Methyl- <i>cis</i> -4-nonene	967.1	970.3	0.64	0.70	20.9
2,2-Dimethyl- <i>trans</i> -3-nonene	984.4	986.3	0.38	0.08	15.2
2,2-Dimethyl- <i>cis</i> -3-nonene	1025.8	1030.8	1.00	1.16	23.7
2,2-Dimethyl- <i>trans</i> -4-nonene	1001.5	1005.1	0.72	0.82	12.9
2,2-Dimethyl- <i>cis</i> -4-nonene	1016.7	1022.6	1.18	1.16	19.5

final treatment of the data, the results for column A were accordingly corrected so that a consistent set of index values would be obtained.

RESULTS AND DISCUSSION

The retention indices were determined at 50, 60, 80 and 100° for all of the compounds studied, and, in addition, at 120° for those of higher boiling points. The relation between I and T did not show any significant deviation from linearity, the maximum differences being within the overall precision of the measurements. For this reason, only the indices for 50 and 100° are tabulated here, together with their temperature coefficients $10 \cdot (dI/dT)$, corresponding to a 10° change in temperature; linear interpolation and extrapolation in the range 50–120° appears to be fully justified.

The retention indices are collected in Tables I–V, grouped according to the hydrocarbon classes. In addition, $10 \cdot (dI/dT)$ values on squalane (SQ) and the differences in retention indices between BTCP and SQ at 100° are given for comparison with this basic non-polar phase; the squalane data were taken (and recalculated when necessary) from the literature^{19–23} and completed by some of my measurements.

The retention-index dispersion, $\Delta I^{BTCP-SQ}$, reflects the selectivity of the BTCP stationary phase. In this respect, the behaviour of alkylbenzenes is the most characteristic. For monosubstituted *n*-alkyl derivatives, ΔI approached a constant value of 119 with lengthening of the alkyl chain. With the di-, tri- and tetra-substituted derivatives, the magnitude of the ΔI values increased with the number of substituents and their proximity, and decreased with the lengthening and branching of the alkyl group; thus, the highest index dispersion was found for 1,2,3,4-tetramethylbenzene and 1,2,3-trimethylbenzene.

The most interesting feature of BTCP, however, is concerned with the temperature dependence of I , and especially for the alkylbenzenes. As may be seen from Table IV, the order of decreasing (dI/dT) values is mono- > di- > tri- > tetra-alkylbenzenes, with a secondary influence of the length and degree of branching of

TABLE IV

RETENTION INDICES OF ALKYL BENZENES ON DI-*n*-BUTYL TETRACHLORO-PHTHALATE AT 50 AND 100°, THEIR TEMPERATURE COEFFICIENTS AND COMPARISON WITH DATA ON SQUALANE

Numbers in parentheses indicate references from which data for squalane are obtained.

Compound	BTCP		$10 \cdot \frac{dI}{dT}$	SQ	BTCP - SQ
	I_{50}	I_{100}		$10 \cdot \frac{dI}{dT}$	
Benzene	774.3	782.9	1.72	2.32 (19)	132.5 (20)
Toluene	886.0	893.0	1.40	2.40 (19)	135.0 (20)
Ethylbenzene	962.0	971.8	1.96	2.62 (19)	124.1 (20)
1,2-Dimethylbenzene	1027.0	1033.3	1.26	2.85 (19)	149.6 (20)
1,3-Dimethylbenzene	989.5	995.0	1.10	2.3 (21)	131.8 (20)
1,4-Dimethylbenzene	995.4	1000.5	1.02	2.47 (19)	138.7 (20)
<i>n</i> -Propylbenzene	1043.0	1055.0	2.40	2.6 (21)	118.9 (20)
Isopropylbenzene	1008.1	1020.0	2.38	2.5 (21)	112.0 (20)
1-Ethyl-2-methylbenzene	1092.2	1101.3	1.82	2.6 (21)	136.6 (20)
1-Ethyl-3-methylbenzene	1058.5	1067.0	1.70	2.2 (21)	118.4 (20)
1-Ethyl-4-methylbenzene	1063.9	1073.7	1.96	2.4 (21)	122.4 (20)
1,2,3-Trimethylbenzene	1168.2	1174.9	1.34	3.2 (24)	163.0 (20)
1,2,4-Trimethylbenzene	1128.6	1132.5	0.78	2.8 (21)	144.3 (20)
1,3,5-Trimethylbenzene	1084.7	1088.0	0.66	2.0 (21)	120.4 (20)
<i>n</i> -Butylbenzene	1142.9	1154.8	2.38	2.4 (21)	119.0 (20)
<i>tert.</i> -Butylbenzene	1068.6	1083.5	2.98	3.0 (24)	110.2 (20)
1- <i>n</i> -Propyl-4-methylbenzene	1144.7	1154.7	2.00	—	115.4 (20)
1-Isopropyl-4-methylbenzene	1104.1	1115.7	2.32	2.7 (23)	104.7 (20)
1,2-Diethylbenzene	1154.4	1163.4	1.80	2.6 (21)	124.3 (20)
1,3-Diethylbenzene	1126.1	1136.4	2.06	2.6 (24)	107.5 (20)
1,4-Diethylbenzene	1138.7	1148.3	1.92	2.9 (24)	109.2 (20)
1-Ethyl-3,4-dimethylbenzene	1189.5	1197.0	1.50	3.0 (24)	125.0 (20)
1-Ethyl-2,4-dimethylbenzene	1186.9	1193.5	1.32	2.9 (24)	126.9 (20)
1-Ethyl-3,5-dimethylbenzene	1146.9	1152.0	1.02	2.6 (24)	103.8 (20)
1-Ethyl-2,5-dimethylbenzene	1187.0	1192.0	1.00	2.8 (24)	132.0 (20)
1,2,3,4-Tetramethylbenzene	1308.2	1312.3	0.82	—	175.1 (23)
1,2,3,5-Tetramethylbenzene	1259.1	1262.6	0.70	3.1 (23)	149.1 (23)
1,2,4,5-Tetramethylbenzene	1257.5	1260.1	0.52	3.1 (23)	152.1 (23)
<i>n</i> -Pentylbenzene	1241.0	1252.5	2.30	2.78 (22)	119.0 (22)

the alkyl substituent. When only compounds with methyl and ethyl substituents are considered, the $10 \cdot (dI/dT)$ increments do not exceed the value of 2, and when compounds with longer and branched alkyls are taken into account the increments do not exceed 3; in all instances, the increments are lower than the corresponding values on squalane. This is a unique property of the tetrahalogenophthalate ester, as with other stationary phases (for which relevant data are available) the (dI/dT) values are of the same, or a higher, order of magnitude as on squalane and (as with squalane) no structural sub-classification can be made. On Carbowax 400, $10 \cdot (dI/dT)$ values have been found to lie between 7.7 (benzene) and 13.6 (1,2,3,4-tetramethylbenzene) from measurements involving all of the C_6 - C_{10} alkylbenzenes²⁵. Values ranging from 6.0 to 7.3 have been obtained²⁶ on Carbowax 1540, from 3.3 to 4.5 on Apiezon L^{27,28}

TABLE V

RETENTION INDICES OF BICYCLIC HYDROCARBONS ON DI-*n*-BUTYL TETRACHLOROPHTHALATE AT 50 AND 100°, THEIR TEMPERATURE COEFFICIENTS AND COMPARISON WITH DATA ON SQUALANE

Compound	BTCP		$10 \cdot \frac{dI}{dT}$	SQ	BTCP - SQ
	I_{50}	I_{100}		$10 \cdot \frac{dI}{dT}$	
<i>trans</i> -Decalin	1088.6	1117.3	5.74	5.0	46.2*
<i>cis</i> -Decalin	1124.6	1155.0	6.08	5.0	45.5*
<i>trans</i> -(1,2)-Octalin	1125.8	1152.4	5.32	—	—
<i>trans</i> -(2,3)-Octalin	1145.0	1170.6	5.12	—	—
(1,9)-Octalin	1130.6	1157.7	5.42	—	—
Tetralin	1274.0	1295.8	4.36	6.5	160.1
<i>cis</i> -Hydrindane	1010.9	1036.3	5.08	4.4*	38.8*
Indane	1152.8	1167.5	2.94	4.1*	149.3*

* Data for squalane from ref. 24, otherwise from ref. 23.

and from 2.2 to 3.6 on SE-30^{5,28}; however, only a limited number of compounds has been investigated in these latter studies.

Table VI provides a summary of the magnitudes of the temperature index increments for different sub-groups of hydrocarbons on BTCP and SQ; here, data for straight-chain mono-olefins are also included, taken from ref. 12 (BTCP) and ref. 8 (SQ). It is clearly seen that the temperature parameter can be of assistance in distinguishing hydrocarbon types. With BTCP, one group of hydrocarbons gives a definite negative slope in dependence of I versus T and several groups give positive slopes of varying magnitude. A particular advantage of BTCP is the difference in the behaviour

TABLE VI

RANGES OF TEMPERATURE INCREMENTS OF RETENTION INDICES FOR DIFFERENT HYDROCARBON TYPES ON DI-*n*-BUTYL TETRACHLOROPHTHALATE AND SQUALANE

Hydrocarbon type	$10 \cdot (dI/dT)$	
	BTCP	SQ
Monoalkylparaffins	0.15-0.65	0.10-0.55
Dialkylparaffins	0.40-0.95	0.35-0.80
Trialkylparaffins	1.10-1.50	0.80-1.10
1-Olefins	0.15-0.20	0.20-0.30
<i>trans</i> -2, <i>trans</i> -3-Olefins	(-)-0.10-(-)0.20	(-)-0.10-(+)0.10
<i>trans</i> -4, <i>trans</i> -5-Olefins	0.15-0.20	0.10-0.50
<i>cis</i> -2, <i>cis</i> -3-Olefins	0.20-0.35	0.20-0.50
<i>cis</i> -4, <i>cis</i> -5-Olefins	0.40-0.55	0.35-0.70
<i>trans</i> -3, <i>trans</i> -4-Isoolefins	0.35-0.70	0.10-0.80
<i>cis</i> -3, <i>cis</i> -4-Isoolefins	0.65-1.20	0.60-1.20
Alkylcyclopentanes	1.80-2.60	1.40-1.80
Alkylcyclohexanes	3.00-4.60	2.20-3.70
Monoalkylbenzenes	1.40-3.00	2.40-3.00
Dialkylbenzenes	1.00-2.30	2.30-2.90
Trialkylbenzenes	0.65-1.50	2.00-3.20
Tetraalkylbenzenes	0.50-0.90	3.00-3.20

of alkylcyclohexanes and alkylbenzenes. These types of compounds frequently occur together in hydrocarbon mixtures, but it is not possible to separate them on the basis of (dI/dT) increments on squalane (nor on other stationary phases for which pertinent data have been published, *cf.* ref. 29), whereas on BTCP they are clearly separable.

Understandably, there is some overlapping of the ranges of increments, and it would not be possible to rely only upon the temperature characteristics in determining the hydrocarbon type; however, even in cases of overlapping ranges, the increments may be of great value as secondary evidence, complementing, for example, the ΔI distribution obtained between squalane, an essentially non-selective phase, and the tetrachlorophthalate as a specific chromatographic phase.

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