Capillary gas chromatography of C_5–C_{13} branched alkynes on squalane and liquid crystal stationary phases

LADISLAV SOJÁK*

Chemical Institute, Comenius University, 842 15 Bratislava (Czechoslovakia)

PAVEL FARKAŠ

Food Research Institute, 825 09 Bratislava (Czechoslovakia)

IVAN OSTROVSKÝ

Chemical Institute, Comenius University, 842 15 Bratislava (Czechoslovakia)

JAROSLAV JANÁK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 642 11 Brno (Czechoslovakia)

and

JACQUES R. CHRÉTIEN

Laboratoire de Chimiométrie, Université d'Orléans, 45067 Orléans Cedex 2, and Institut de Topologie et de Dynamique des Systèmes, Université Paris VII, associé au CNRS, 75005 Paris (France)

ABSTRACT

The retention behaviour of 49 C_5–C_{13} branched alkynes, including all 36 methyl- and dimethylalkynes up to C_8, were studied by capillary gas chromatography on squalane and 4-*n*-pentylacetophenone-O-(4-*n*-pentyloxybenzoyl)oxime liquid crystal as stationary phases. An additive method of retention increments based on the analogy of retention in homologous series of the corresponding branched alkynes and alkenes, showing an average precision of 1 index unit, was suggested for the calculation of retention indices of branched alkynes and alkynes with a methyl group on the α-carbon in particular. Both regularities and anomalies in the retention behaviour of branched alkynes are discussed with regard to retention–structures correlations. The advantages of liquid crystals as stationary phases for the separation of isomers with close physico-chemical characteristics are pointed out.

INTRODUCTION

Alkynes are intermediates in a number of organic syntheses. They are produced at low concentrations as the by-products of processes of catalytic and thermal conversions of hydrocarbons and, owing to their high reactivity, they can affect further processing of the products.

Capillary gas chromatography of straight-chain alkynes has been studied in considerable detail for compounds with a wide range of carbon numbers, up to C_{20} [1–9]. However, the retention behaviour of branched-chain alkynes has not been studied. Only Hively and Hinton [1] have published, among the retention indices of other hydrocarbons, also those of 4-methyl-1-pentyne and 5-methyl-1-hexyne on

squalane. Starting from previous studies of the retention behaviour of hydrocarbons of various types, the aim of this work was to characterize the retention behaviour of branched alkynes on squalane and 4-*n*-pentylacetophenone(O-4-*n*-pentyloxybenzoyl) oxime (PBO) liquid crystal, *i.e.*, in systems in which we earlier studied retention behaviour of straight-chain alkynes [2].

EXPERIMENTAL

The PBO nematic liquid crystal, having a mesophase range of 63–94°C and possible supercooling to 27°C, was synthesized by Dr. W. Weissflog, Martin Luther University (Halle, Germany).

Model mixtures of branched alkynes were prepared from 24 different C_5–C_{13} branched alkynes which were prepared by acetylene alkylation in liquid ammonia for the less crowded compounds or donated by Dr. L. Miginiac (University of Poitiers, France). A further fifteen C_7 and C_8 branched alkynes were prepared as mixed standards by the methylene group insertion reaction (MIR) [10] in molecules of *n*-alkynes and branched alkynes.

Model mixtures of alkynes were separated on a 107 m × 0.25 mm I.D. glass capillary column coated with squalane with a film thickness of 0.40 μm at an inlet pressure of 0.26 MPa and a linear velocity of hydrogen carrier gas of 36 cm s^{-1}, with an efficiency $n = 360\ 000$, or $n_{eff} = 260\ 000$ plates for 1-nonyne with $k = 5.4$ at 80°C. The parameters of the capillary column with the PBO liquid crystal were 106 m × 0.25 mm I.D. inlet pressure of hydrogen carrier gas 0.20 MPa and linear velocity was 21 cm s^{-1}, with an efficiency $n = 360\ 000$ or $n_{eff} = 214\ 000$ plates for 1-nonyne with $k = 1.5$ at 80°C.

An adapted Perkin-Elmer F-11 gas chromatograph and a Fractovap 4200 (Carlo Erba) with flame ionization detectors were used to measure retention characteristics. The thermostat temperature was maintained with a precision of ±0.1°C with a calibrated glass thermometer. Samples were injected onto the column with a 1-μl syringe with the aid of a splitter with a splitting ratio of 1:100 so that a sample size range of 10^{-9}–10^{-10} g for of each component could be obtained. Retention times were measured from the methane peak maximum with a precision of 0.1 s. The measurement repeatability of retention indices expressed in terms of the standard deviation of the arithmetic mean was ±0.03 index unit (i.u.) on squalane and ±0.05 i.u. on PBO.

RESULTS AND DISCUSSION

Table I shows the retention indices of C_5–C_{13} branched alkynes and their temperature dependence measured on squalane and PBO liquid crystal with synthesized individual standards (denoted s) or mixed products from MIR (r). Table I also gives the retention indices of alkynes up to C_8 calculated for a temperature of 40°C (c). Table I is supplemented with retention indices of C_6–C_{13} straight-chain alkynes measured under the same conditions as those used previously [2]. They serve for comparison of the retention data of branched- and straight-chain alkynes or were used to calculate the retentions of branched alkynes.

The comparison of the measured and published [1] retention indices for 4-

TABLE I

RETENTION INDICES AND THEIR TEMPERATURE COEFFICIENTS $\mathrm{d}I/\mathrm{d}T$ FOR C_5–C_{13} AL-
KYNES ON SQUALANE (SQ) AND PBO LIQUID CRYSTAL

The calculated values of retention indices of branched alkynes (c) are valid for the temperature of 40°C.
$\mathrm{d}I^{SQ}/\mathrm{d}T$ values of C_5–C_8 alkynes were measured in the temperature range 40–60°C and those of C_9–C_{13}
alkynes at 70–90°C; $\mathrm{d}I^{PBO}/\mathrm{d}T$ values of C_5–C_8 alkynes were measured at 40–60°C, those of C_9–C_{13} alkynes
at 80–90°C.

Alkyne		I^{SQ}_{80}	$\mathrm{d}I^{SQ}/\mathrm{d}T$	I^{PBO}_{80}	$\mathrm{d}I^{PBO}/\mathrm{d}T$	ΔI^{PBO-SQ}
3-Methyl-1-butyne	s	435.5	0.00	512.8	−0.07	77.6
3,3-Dimethyl-1-butyne	s	467.1	0.00	525.9	0.01	58.9
3-Methyl-1-pentyne	c	539.4	−	−	−	−
4-Methyl-1-pentyne	s	550.3	0.02	633.2	0.04	82.9
1-Hexyne	s	583.4	0.01	678.0	0.08	94.6
3,3-Dimethyl-1-pentyne	c	589.3	−	−	−	−
4-Methyl-2-pentyne	c	594.2	−	−	−	−
4,4-Dimethyl-1-pentyne	r	600.3	0.09	−	−	−
4,4-Dimethyl-2-pentyne	s	611.6	−0.12	658.4	0.20	46.8
3-Hexyne	s	623.1	−0.09	692.8	0.05	69.7
3,4-Dimethyl-1-pentyne	r	623.5	0.07	−	−	−
3-Methyl-1-hexyne	r	634.3	0.02	−	−	−
2-Hexyne	s	640.3	−0.04	718.9	0.05	78.6
5-Methyl-1-hexyne	r	653.6	0.05	−	−	−
4-Methyl-1-hexyne	r	659.3	0.07	−	−	−
2-Methyl-3-hexyne	s	660.2	−0.12	713.2	0.15	53.0
2,2-Dimethyl-3-hexyne	s	674.6	−0.15	707.1	0.17	32.5
3,3-Dimethyl-1-hexyne	c	678.8	−	−	−	−
1-Heptyne	s	683.6	0.01	779.1	0.06	95.5
2,5-Dimethyl-3-hexyne	s	688.9	−0.16	723.2	0.10	34.2
3,5-Dimethyl-1-hexyne	c	689.6	−	−	−	−
4-Methyl-2-hexyne	c	689.8	−	−	−	−
2,2,5-Trimethyl-3-hexyne	s	695.6	−0.18	707.8	0.05	12.3
5,5-Dimethyl-1-hexyne	c	699.6	−	−	−	−
5-Methyl-2-hexyne	s	701.2	−0.03	771.0	0.22	69.8
3-Heptyne	s	717.3	−0.07	782.4	0.09	65.1
4,4-Dimethyl-1-hexyne	c	717.9	−	−	−	−
4,4-Dimethyl-2-hexyne	s	719.5	−0.09	767.1	0.32	47.7
3,4-Dimethyl-1-hexyne	c	726.7	−	−	−	−
3-Methyl-1-heptyne	r	730.1	0.01	−	−	−
4,5-Dimethyl-1-hexyne	c	735.1	−	−	−	−
5,5-Dimethyl-2-hexyne	r	740.0	0.00	−	−	−
2-Heptyne	s	743.0	−0.03	820.4	0.16	77.4
4-Methyl-1-heptyne	r	749.9	0.05	−	−	−
6-Methyl-1-heptyne	r	749.9	0.03	−	−	−
2-Methyl-3-heptyne	s	752.6	−0.10	800.3	0.12	47.7
5-Methyl-1-heptyne	r	759.7	0.07	−	−	−
5-Methyl-3-heptyne	r	756.9	−0.07	−	−	−
4,5-Dimethyl-2-hexyne	r	760.4	−0.03	−	−	−
6-Methyl-3-heptyne	s	776.7	−0.04	833.4	0.22	55.9
4-Methyl-2-heptyne	r	780.6	−0.07	−	−	−
1-Octyne	s	783.0	0.02	879.4	0.06	96.4
4,4,5-Trimethyl-2-hexyne	s	806.01	−0.02	849.7	0.38	43.6
4,4-Dimethyl-2-heptyne	s	806.5	−0.12	850.4	0.31	43.9
6-Methyl-2-heptyne	r	807.8	−0.02	−	−	−
5-Methyl-2-heptyne	r	811.1	0.00	−	−	−

TABLE I (*continued*)

Alkyne		I_{80}^{SQ}	dI^{SQ}/dT	I_{80}^{PBO}	dI^{PBO}/dT	ΔI^{PBO-SQ}
4-Octyne	s	811.3	−0.05	872.1	0.14	60.8
6,6-Dimethyl-3-heptyne	s	813.6	−0.01	856.6	0.35	43.0
5,5,4-Trimethyl-2-hexyne	s	816.5	0.01	863.2	0.45	46.7
3-Octyne	s	818.0	−0.06	880.5	0.17	62.5
2,2,6-Trimethyl-3-heptyne	s	822.7	−0.09	838.6	0.30	15.9
4-Ethyl-4-methyl-2-hexyne	s	825.3	−0.06	873.1	0.40	47.8
2-Octyne	s	842.3	−0.04	920.7	0.18	68.4
2,2,6,6-Tetramethyl-3-heptyne	s	857.4	−0.03	861.6	0.41	4.3
1-Nonyne	s	883.3	0.02	980.2	0.08	96.9
2,2,5-Trimethyl-5-ethyl-3-heptyne	s	905.8	−0.06	896.0	0.26	−9.8
4-Nonyne	s	910.4	−0.04	967.7	0.20	57.3
2,2,5,6,6-Pentamethyl-3-heptyne	s	914.4	−0.01	908.8	0.41	−5.6
3-Nonyne	s	916.0	−0.06	980.2	0.18	64.2
2,7-Dimethyl-4-octyne	s	929.6	0.00	973.5	0.38	43.9
2-Nonyne	s	941.0	−0.03	1019.1	0.20	78.1
2,2,5,5,6,6-Hexamethyl-3-heptyne	s	956.4	0.04	938.7	0.47	−17.7
1-Decyne	s	983.2	0.02	1080.8	0.18	97.6
2,2,7,7-Tetramethyl-4-octyne	s	1003.4	0.08	1024.5	0.52	21.1
4-Decyne	s	1007.3	−0.03	1067.5	0.41	60.2
5-Decyne	s	1008.2	−0.02	1064.9	0.48	56.7
3-Decyne	s	1014.3	−0.05	1079.0	0.36	64.7
2-Decyne	s	1041.1	−0.03	1120.6	0.34	79.5
1-Undecyne	s	1083.3	0.02	1181.4	0.14	98.1
5-Undecyne	s	1104.2	−0.01	1161.5	0.53	57.3
4-Undecune	s	1104.8	−0.02	1164.7	0.48	59.9
3-Undecyne	s	1113.5	−0.04	1178.3	0.44	64.8
2-Undecyne	s	1140.9	−0.02	1220.7	0.35	79.8
1-Dodecyne	s	1183.3	0.02	1282.2	0.15	98.9
6-Dodecyne	s	1199.6	0.00	1258.2	0.58	58.6
5-Dodecyne	s	1201.1	−0.02	1258.2	0.58	57.1
4-Dodecyne	s	1203.3	−0.03	1263.1	0.50	59.8
3-Dodecyne	s	1212.5	−0.05	1277.6	0.44	65.1
2-Dodecyne	s	1240.8	−0.03	1321.0	0.36	80.2
1-Tridecyne	s	1283.4	0.02	1382.9	0.15	99.5
6-Tridecyne	s	1295.6	0.01	1353.4	0.64	57.8
5-Tridecyne	s	1298.5	0.01	1355.8	0.62	57.3
4-Tridecyne	s	1301.5	−0.01	1361.6	0.53	60.1
3-Tridecyne	s	1311.9	−0.04	1377.1	0.44	65.2
2-Tridecyne	s	1340.6	−0.02	1421.2	0.38	80.6

methyl-1-pentyne and 5-methyl-1-hexyne on squalane suggests that the retention indices measured by us are lower by 2.6 and 2.1 i.u., respectively. This is in accord with our previous finding that for unsaturated hydrocarbons the retention indices from ref. 1 are systematically higher, *e.g.*, for C_6 C_8 aromatic hydrocarbons by 3.3 i.u. on average.

Retention of branched alkynes on squalane

As we had only a limited number of standard alkynes at our disposal for characterizing the retention behaviour of branched alkynes, we studied the possibility of calculating their retentions. As far as the compounds with more functional groups in

their molecules such as branched alkynes are concerned, their retention indices may be calculated from the sum of contributions of homomorphic factors of separate functional groups under the assumption that they do not affect one another [11]. The measured values of retention indices of branched alkynes were used to investigate the additivity of contributions of functional groups of branched alkynes, *i.e.*, of triple bond and methyl branching, on the basis of known retention indices of *n*-alkynes [2] and of branched alkanes [12] on squalane. We started from the concept that the branched alkyne molecule consists of structural elements of the coresponding *n*-alkyne and branched alkane. The homomorphic factor which characterizes the contribution of the functional groups to the retention index is defined as follows [12]:

$$H = I_i - I_z \tag{1}$$

where I_i is the retention index of sample compound i and I_z is the retention index of the corresponding *n*-alkane with the same carbon skeleton on the given stationary phase and at the given temperature. H values for branched alkynes are given by

$$H_{\text{alkyne}} = H_{n\text{-alkyne}} + H_{\text{branched alkane}} \tag{2}$$

On the basis of eqns. 1 and 2, the calculated values of the retention indices for 36 C_5–C_8 branched alkynes agreed with those measured on squalane in the range from -64.7 to $+2.3$ i.u. The difference between the measured and the calculated retention indices of branched alkynes on squalane, $\sigma I = I_m - I_c$, depends on the position of the methyl group with respect to the triple bond, on the position of the triple bond in the chain and on the number of carbon atoms in the molecule of the particular alkyne.

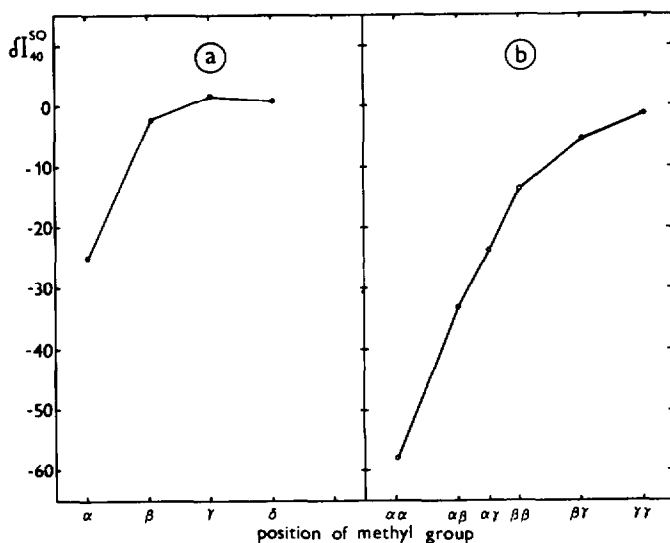Fig. 1 illustrates the dependences of σI on the position of one and two methyls

Fig. 1. Dependence of difference between measured and calculated retention indices of (a) methyl- and (b) dimethylalkynes on squalane at 40°C on the position of the methyl groups with respect to the triple bond.

with respect to the triple bond. For the methyl groups on the carbon atom neigh-
bouring the triple bond, the calculated retention indices of alkynes are higher by 25
and 58 i.u. than the measured values. As the distance of the methyl group from the
triple bond increases, the value of σI approaches zero. The dependence of σI on the
position of the triple bond for methylheptynes and dimethylhexynes in Fig. 2 il-
lustrates a characteristic increase in negative σI values with shift of the triple bond
towards the centre of the alkyne molecule. The influence of the number of carbon
atoms on σI in Fig. 3 illustrates the decrease in negative σI values with increasing
number of carbon atom in 3,3-dimethyl-1-alkynes.

The retention indices calculated for monomethylalkynes according to eqns. 1
and 2 agree with the measured values within few units if methyl branching is separat-
ed from the triple bond by at least one CH_2 group, but the agreement diminishes with
shift of the triple bond towards the chain centre (Fig. 2). For dimethylalkynes the
agreement of σI is within a few units if both methyl groups are separated from the
triple bond by at least two CH_2 groups (Fig. 1b). Limits of the calculation of reten-
tion indices of branched alkynes by eqns. 1 and 2 are illustrated by the fact that the
calculation does not differentiate 3-methyl-1-hexyne and 4-methyl-1-hexyne although
their retention indices on squalane differ by 23 i.u.

On the basis of this evaluation, we propose a different procedure based on the
similarity of retention in homologous series of the corresponding branched alkynes
and alkenes (whose retention indices on squalane up to C_8 are known [11–16], for
calculation of the retentions of branched alkynes up to C_8 with methyl branching on
the carbon atom neighbouring the triple bond (and also for other alkynes). The
homomorphic factor of an alkyne was calculated from the relationship

$$H_{\text{alkyne}} = H_{\text{alkene}} + \delta H_1 + \delta H_2 \tag{3}$$

where H is the homomorphic factor of the branched alkyne or alkene with the same
carbon atom skeleton on squalane at the given temperature. σH_1 expresses the differ-
ence between the homomorphic factors for n-alkyne and n-alkene with the same
position of the multiple bond and with the same number of carbon atoms as in the
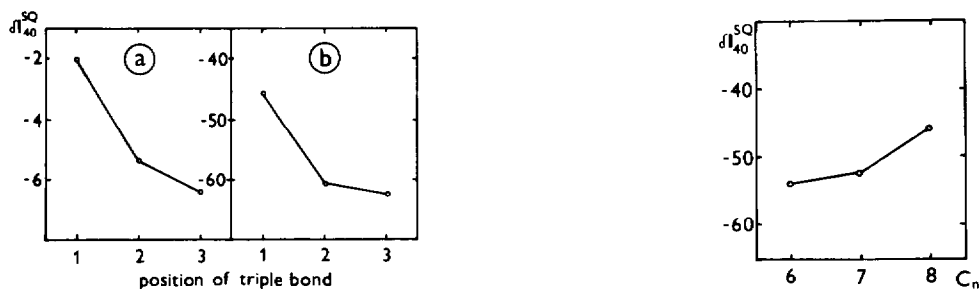main chain of the branched hydrocarbon:

Fig. 2. Dependence of difference between measured and calculated retention indices on squalane at 40°C
for (a) methylheptynes with the methyl group on the β-carbon and (b) dimethylhexynes with two methyl
groups on the α-carbon.

Fig. 3. Dependence of difference between measured and calculated retention indices on squalane at 40°C on
the number of carbon atoms for 3,3-dimethyl-1-alkynes.

$$\delta H_1 = H_{n\text{-alkyne}} - H_{n\text{-alkene}} \tag{4}$$

σH_2 expresses different effect of an alkyl group in the side chain in the molecule of the branched alkyne on retention in comparison with the corresponding alkene. It may be calculated from the known values of retention indices of branched alkynes and alkenes with the same carbon atom skeleton and with the same position of the multiple bond:

$$\delta H_2 = H_{\text{alkyne}} - H_{\text{alkene}} - \delta H_1 \tag{5}$$

σH_2 values characterize the given structure in the given homologous series similarly to σH_1 values. Therefore, for the calculation of σH_2 it is sufficient to know the retention of one member of the given homologous series of alkynes.

For the homologous series of 3-methyl-1-alkynes we only measured the retention index of 3-methyl-1-butyne. On the basis of eqn. 3, from the known retention indices of 3-methyl-1-alkynes we calculated the retention indices of further 3-methyl-1-alkynes up to C_8. The σH_1 value was considered for the 1-butyne–1-butene pair to be $\sigma H_1^{SQ} = -2.9$ i.u. and the value of $\sigma H_2^{SQ} = -11.7$ i.u. was calculated from the homomorphic factors for 3-methyl-1-butyne (-64.5) and 3-methyl-1-butene (-49.9). We compared the retention indices for 3-methyl-1-hexyne and 3-methyl-1-heptyne calculated in this way with those measured experimentally in the case of products from the reaction of methylene group insertion into the molecule of corresponding 1-alkynes. The agreement of 0.5 i.u. suggests a high precision of the calculation of retention by this procedure for structures with methyl branching on the carbon atom neighbouring the triple bond.

Retention indices of other branched alkynes up to C_8 for which the retention index of only one member of the homologous series was known, *i.e.* of 4-methyl-1-alkynes, 5-methyl-1-alkynes, 5-methyl-2-alkynes, 3,3-dimethyl-1-alkynes and 4,4-dimethyl-1-alkynes, were calculated in a similar way.

For 6-methyl-1-heptyne, where no retention index was available for any of the members of the homologous series, in the calculation of its retention index we started from the σH_2 value which we obtained by extrapolation of the dependence of σH_2 on the position of the methyl group in the side chain in relation to the multiple bond in position 1. For this we started from the assumption that σH_2 would approach zero as the methyl group became increasingly isolated from the multiple bond. The value of the retention index of 6-methyl-1-heptyne calculated in this way was 1.6 i.u. higher than that measured for the product of MIR (according to eqn. 2 the retention index was lower by 1.0 i.u.).

For 6-methyl-2-heptyne we also derived the contribution of σH_2 to retention in a similar way to 6-methyl-1-heptyne by extrapolating the dependence of σH_2 values for methyl-2-alkynes and -alkenes with increasing distance of the methyl group from the multiple bond. The retention index calculated in this way was 2.3 i.u. higher than the measured value (according to eqn. 2 higher by 0.5 i.u.).

The contribution of σH_2 to the retention of 4-methyl-2-alkynes (α-methyl-2-alkynes) was found by interpolating σH_2 values for α-methyl-1-alkynes and α-methyl-3-alkynes. The calculated retention index for 4-methyl-2-heptyne was 1 i.u. lower than the measured value (the calculated value according to eqn. 2 is 27.9 i.u. higher than the measured value.
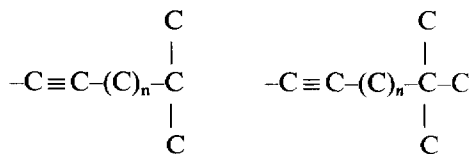
The contribution of σH_2 to the retention of 3,4-dimethyl-1-pentyne (α,β-di-methyl-1-alkyne) was calculated as the sum of the contributions of σH_2 for 3-meth-yl-1-pentyne (α-methyl-1-alkyne) and 4-methyl-1-pentyne (β-methyl-1-alkyne). The calculated retention index for 3,4-dimethyl-1-pentyne is 3.8 i.u. higher than the mea-sured value for the MIT product (according to eqn. 2 higher þy 34.4 i.u.). The value of σH_2 back-calculated for α,β-dimethyl-1-alkynes was used to calculate the retention index of 3,4-dimethyl-1-hexyne (the retention index calculated by eqn. 2 was higher by 25.0 i.u.).

For 4,4-dimethyl-1-pentyne, 5,5-dimethyl-2-hexyne and 5-methyl-3-heptyne none of the procedures based on eqn. 3 could be used to calculate their retention indices with acceptable precision. As they are alkynes in which dimethyl branching is separated from the triple bond by one CH_2 group and methyl branching occurs on the carbon atom neighbouring the triple bond, calculation of their retention indices according to eqn. 2 is not precise enough. Their retention indices were measured experimentally from peaks of the MIR mixture if all other reaction products were identified (retention indices calculated according to eqn. 2 were 12.6, 20.8 and 32.4 i.u., respectively, higher).

Of 44 possible isomers of branched alkynes up to C_8, all 36 methyl- and di-methylalkynes were thus characterized (26 by the measurements and 10 by calcula-tion of retention indices). Retention indices of ethylalkynes and trimethylalkynes could neither be calculated by the above procedures according to eqn. 3 nor, because of a lack of starting substances, be obtained by MIR reaction. As their structures contain ethyl and methyl branching in the neighbourhood of the triple bond, the calculation of their retention indices by eqn. 2 is not sufficiently precise.

Values of homomorphic factors of branched alkynes up to C_8 on squalane at 40°C depending on the number of carbon atoms in various homologous series for monomethyl- and dimethylalkynes are illustrated in Figs. 4 and 5. In comparison with straight-chain alkynes, branching of the carbon chain causes a considerable decrease in retention depending on the degree of branching, position of the methyl group with respect to the triple bond and the number of carbon atoms in the alkyne molecule. Isomers of branched alkynes with the methyl group on the α-carbon next to the triple bond show the lowest retention. With increasing distance of the methyl from the triple bond the retentions of individual isomers increase.

In contrast to *n*-alkynes for which the first members of their homologous series show higher H values, the first members of the series of branched alkynes often have relatively lower H values. This lower retention can be observed, *e.g.*, for 3-methyl-1-butyne and 5-methyl-2-hexyne (Fig. 4), 3,3-dimethylbutyne and 4.4-dimethyl-2-pen-tyne (Fig. 5) and other alkynes. A common structural feature of the branched alkynes showing such behaviour is the presence of a quaternary or tertiary carbon at the end of the chain, *i.e.*, the following structures:
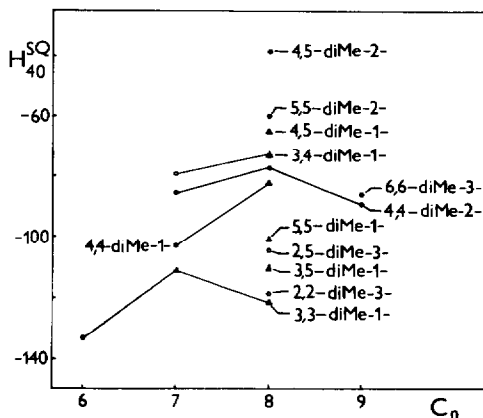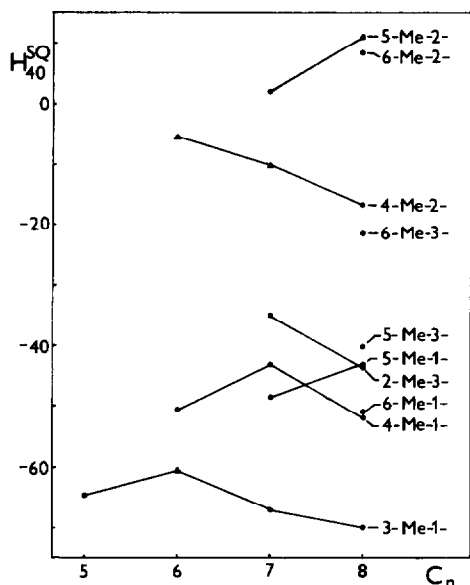
$$
\begin{array}{ccccc}
& C & & & C \\
& | & & & | \\
-C \equiv C-(C)_n-C & & & -C \equiv C-(C)_n-C-C \\
& | & & & | \\
& C & & & C \\
\end{array}
$$

Fig. 4. Dependence of H_{40}^{SQ} on the number of carbon atoms for homologous series of C_5–C_8 mono-methylalkynes on squalane at 40°C. 4-Me-1 = 4-Methyl-1-alkyne, etc. $\bigcirc$ = Measured values; $\triangle$ = calculated values.

Fig. 5. Dependence of H_{40}^{SQ} on the number of carbon atoms for homologous series of C_6–C_9 dimethy-lalkynes on squalane at 40°C. 3,3-diMe-1- = 3,3-Dimethyl-1-alkyne, etc. $\bigcirc$ = Measured values; $\triangle$ = calculated values.

A higher symmetry of the molecule and hence also lower polarizability and weaker solute–solvent interactions are characteristic of these structures. In accord with this, the retention for 5-methyl-1-hexyne is anomalously lower than that for 4-methyl-1-hexyne and similarly for 6-methyl-1-heptyne in comparison with 5-meth-yl-1-heptyne. A similar effect was found previously [17] also for branched alkanes, which suggests its general validity also for other branched hydrocarbons.

The dependence of the temperature coefficients of retention indices, dI/dT, on the number of hydrocarbon atoms for C_5–C_8 monomethylalkynes on squalane is shown in Fig. 6. It is obvious that the dI/dT values for monomethyl-1-alkynes are positive, similarly to those for linear 1-alkynes, in the range 0.00–0.07 i.u./°C. Simi-larly to linear alkynes, the dI/dT values for monomethylalkynes with the triple bond situated inside the chain are negative, in the range 0.00 to -0.12 i.u./°C.

Comparing the dependences dI/dT (C_z) and H (C_z) for homologous series of monomethylalkynes, we can observe a certain similarity. In both instances the values mentioned above reach more positive values as the distance of the methyl group in the side-chain from the triple bond increases. Anomalously lower are also the dI/dT values for structures with a quaternary or tertiary carbon atom at the end of the chain. These results agree with the fact that more symmetrical structures have lower dI/dT values. Similarly to straight-chain alkynes, the dI/dT values become more negative as the triple bond moves along the carbon chain of branched alkynes from position 1 to 3. Similar dependences between structure and dI/dT values were also found for C_6–C_9 dimethylalkynes.
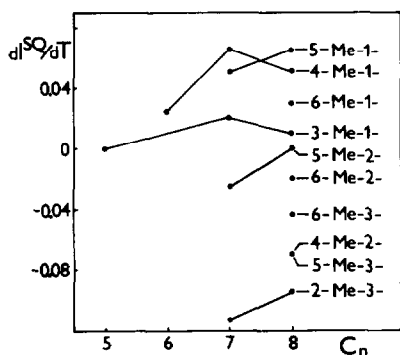
Fig. 6. Dependence of $\mathrm{d}I^{SQ}/\mathrm{d}T$ on the number of carbon atoms for C_5–C_8 monomethylalkynes on squalane.

Retention of branched alkynes on PBO

The previous study [2] of the retention behaviour of straight-chain alkynes on PBO illustrated the advantage of liquid crystals as stationary phases for the separation of isomeric *n*-alkynes, particularly those with a central position of triple bond. For instance, for a quantitative separation of the pairs 5-and 4-decyne and 5- and 4-undecyne on squalane, 875 000 and 1 200 000 plates, respectively, are required, but on PBO the required plate numbers were an order of magnitude lower. The selectivity of the liquid crystal for isomeric *n*-alkynes increases with the shift of the triple bond from the centre of the molecule towards end of the carbon chain, hence in the same direction in which the isomers are eluted. Therefore, the conditions for their separation are also milder on the liquid crystal. In the separation of isomers with a central position of the triple bond from their neighbouring positional isomers, the different orientations of the ends of the zig-zag carbon chain in the molecules of the two types of isomer have a marked effect. The isomer that has the end of the zig-zag chain oriented in the direction of the molecular axis, which leads to a more stretched molecule (a greater molecular length-to-width ratio) has an increased retention on the liquid crystal. This is manifested, for instance, with *n*-decynes as a reversed retention sequence of 5- and 4-decynes on PBO in comparison with that on squalane.

Retention indices of various synthesized C_5–C_{13} branched alkynes on PBO liquid crystal are listed in Table I. For the calculation of retention indices of other branched alkynes according to eqns. 2 and 3 the required retention indices of corresponding alkanes and alkenes on PBO are missing.

The retention of branched alkynes on PBO, owing to its selectivity for the length-to-width ratio of the solute molecule, is, in comparison with retention on squalane, determined more markedly by the degree of alkyne branching. At the same time, as result of the polarity of PBO, dipole–dipole interactions also appear. With increasing branching of the alkyne molecule as result of decreasing molecule length-to-width ratio and with increasing shielding of the triple bond, the retentions of alkynes on PBO decrease in comparison with those on squalane in a corresponding way. This is demonstrated by the difference in retention indices, ΔI_{80}^{PBO-SQ}, of alkyl-3-heptynes in Table II. The shielding effect of methyl groups and the decrease in linearity of the molecules of strongly branched alkynes manifests itself in a lower value of

TABLE II

VALUES OF $\Delta I^{\text{PBO}-\text{SQ}}$ FOR 3-HEPTYNE AND METHYL-3-HEPTYNE AT 80°C

Alkyne	$\Delta I_{80}^{\text{PBO}-\text{SQ}}$
3-Heptyne	65.1
2-Methyl-3-heptyne	47.7
6,6-Dimethyl-3-heptyne	43.0
2,2,6-Trimethyl-3-heptyne	15.9
2,2,6,6-Tetramethyl-3-heptyne	4.3
2,2,5,6,6-Pentamethyl-3-heptyne	−5.6
2,2,5,5,6,6-Hexamethyl-3-heptyne	−17.7

their retention indices on PBO in comparison with those on squalane: *e.g.*, for 2,2,5,5,6,6-hexamethyl-3-heptyne $\Delta I^{\text{PBO}-\text{SQ}} = -17.7$ i.u.

The contribution of the methyl group in the alkyne side-chain to retention on PBO depends, in the first place, on the position with respect to the triple bond. The methyl group closer to the triple bond has a stronger shielding effect on the triple bond and hence also on the dipole–dipole interaction, which is reflected in lower values of $\Delta I^{\text{PBO}-\text{SQ}}$ (Table III). However, as shown by retention measurements on isomeric methylalkanes on PBO, the contribution of the shape of the molecule to the retention on the liquid crystal also decreases in the same direction.

The contribution of the methyl group in the alkyne side-chain to the retention on PBO depends, in comparison with squalane, on the position of the triple bond in the chain and on the number of carbon atoms in the molecule to a relatively smaller extent. This is proved by the values of $\Delta\Delta I^{\text{PBO}-\text{SQ}}$ (Table IV), calculated as

$$\Delta\Delta I^{\text{PBO}-\text{SQ}} = \Delta I_{\text{b}} - \Delta I_{\text{n}} \tag{6}$$

where

$$\Delta I_{\text{b}} = I_{\text{b}}^{\text{PBO}} - I_{\text{b}}^{\text{SQ}}$$

b being the branched alkyne and

$$\Delta I_{\text{n}} = I_{\text{b}}^{\text{PBO}} - I_{\text{n}}^{\text{SQ}}$$

n being the straight-chain alkyne with the same number of carbon atoms and with the same position of the triple bond as in the main chain of the branched alkyne.

TABLE III

VALUES OF $\Delta I^{\text{PBO}-\text{SQ}}$ FOR ALKYL-3-HEPTYNES AND 3-HEXYNE AT 80°C

Alkyne	$\Delta I_{80}^{\text{PBO}-\text{SQ}}$
2-Methyl-3-heptyne	47.7
6-Methyl-3-heptyne	55.9
2,2-Dimethyl-3-hexyne	32.5
6,6-Dimethyl-3-heptyne	43.0

TABLE IV

THE VALUES OF $\Delta\Delta I^{PBO-SQ}$ FOR BRANCHED ALKYNES WITH THE SAME POSITION OF METHYL GROUPS TOWARDS THE TRIPLE BOND AT 80°C

Alkyne	Number of C atoms	Position of methyl group	$\Delta\Delta I_{80}^{PBO-SQ}$
3-Methyl-1-butyne	5	α	-15.0
2-Methyl-3-hexyne	6	α	-16.7
2-Methyl-3-heptyne	7	α	-17.4
5-Methyl-2-hexyne	7	β	-8.8
6-Methyl-3-heptyne	8	β	-9.2
3,3-Dimethyl-1-butyne	6	α,α	-33.7
4,4-Dimethyl-2-pentyne	7	α,α	-31.2
4,4-Dimethyl-2-hexyne	8	α,α	-30.9
4,4-Dimethyl-2-heptyne	9	α,α	-33.5

It is obvious from Table IV that the values of $\Delta\Delta^{PBO-SQ}$ for alkynes with the methyl group on the α-carbon are approximately double those for alkynes with the methyl group on the β-carbon and for alkynes with two methyl groups on the α-carbon, and they are approximately double those for alkynes with one methyl group on the α-carbon.

On the basis of the above correlations, it is possible, to a certain extent, to predict the retention indices of branched alkynes on PBO from the measured retention indices of straight-chain alkynes on PBO and squalane, and from those for branched alkynes on squalane.

The temperature coefficients of the retention indices of C_5-C_{13} branched alkynes on PBO are positive (3-methyl-1-butyne is an exception with -0.07 i.u./°C) in the range 0.01–0.52 i.u.,/°C, and are higher than those on squalane. Positional 1-alkynes show the lowest dI/dT values. The dI/dT values of other branched alkynes change as a function of the position of the triple bond in the main chain, on the degree of branching and on the positions of methyl groups in side-chain with respect to the triple bond.

The selectivity of liquid crystal stationary phases for the separation of isomeric branched alkynes was used in the separation of 6-methyl-1-heptyne and 4-methyl-1-
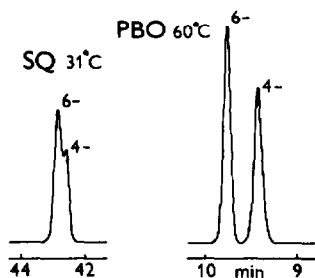

Fig. 7. Separation of 4-methyl-1-heptyne (4-) and 6-methyl-1-heptyne (6-) on a capillary column with squalane and PBO liquid crystal.

heptyne, which have similar retentions on squalane ($\sigma I_{48}^{SQ} = 0.8$ i.u.). As can be seen from Fig. 7, the separation of these isomers is substantially easier on the liquid crystal and the sequence remains unchanged, which suggests a more selective retention of 6-methyl-1-heptyne, in accordance with the above expectations.

The knowledge obtained in the separation and characterization of alkynes was used for the analysis of alkynes in the C_5 fraction from the pyrolysis of higher hydrocarbons and from catalytic dehydrogenation of n-heptane.

REFERENCES

1 R. A. Hively and R. E. Hinton, *J. Gas Chromatogr.*, 6 (1968) 203.
2 L. Soják, P. Farkaš, J. Janák, S. Rang and O. Eisen, *J. Chromatogr.*, 287 (1984) 271.
3 W. Meltzov, S. Warwel and B. Fell, *Chromatographia*, 6 (1973) 183.
4 R. Riedo, D. Fritz, G. Tarján and E. Kováts, *J. Chromatogr.*, 126 (1976) 63.
5 S. Rang, K. Kuningas, A. Orav and O. Eisen, *J. Chromatogr.*, 119 (1976) 451.
6 S. Rang, K. Kuningas, A. Orav and O. Eisen, *J. Chromatogr.*, 128 (1976) 53 and 59.
7 G. Dielmann, *Dissertation*, Ruhr-Universität, Bochum, 1977.
8 Th. Welsch, W. Engewald and P. Berger, *Chromatographia*, 1 (1978) 5.
9 S. Rang, O. Eisen, A. V. Kiselev, A. E. Meister and K. D. Scherbakova, *Chromatographia*, 7 (1979) 327.
10 I. Dvoretzky, D. B. Richardson and L. R. Durret, *Anal. Chem.*, 4 (1963) 545.
11 G. Schomburg, *J. Chromatogr.*, 23 (1966) 1.
12 J. A. Rijks and C. A. Cramers, *Chromatographia*, 7 (1974) 215.
13 D. A. Tourres, *J. Gas Chromatogr.*, 5 (1967) 35.
14 J. C. Loewenguth and D. A. Tourres, *Fresenius' Z. Anal. Chem.*, 236 (1968) 170.
15 A. Matukuma, in C. L. A. Harbourn (Editor), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, p. 55.
16 L. Soják and A. Bučinská, *J. Chromatogr.*, 51 (1970) 75.
17 L. Soják, unpublished results.