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CAPILLARY GAS CHROMATOGRAPHY OF *n*-ALKYNES ON SQUALANE AND A LIQUID CRYSTAL AS STATIONARY PHASES

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SUMMARY

The elution behaviour of 43 possible C₆-C₁₄ *n*-alkynes was studied on squalane and 4-*n*-pentylacetophenone-(O-4-*n*-pentyloxybenzoyloxime) liquid crystal as stationary phases in glass capillary columns. The influence of factors affecting the reproducibility of the retention indices of *n*-alkynes was investigated. Structure-retention correlations are discussed as a means of characterization, considering fine structural effects (propyl effect, hyperconjugation, alternation). Advantages of the use of a liquid crystal as a stationary phase for the separation of *n*-alkyne isomers are demonstrated.

INTRODUCTION

The retention behaviour of *n*-alkyne isomers in capillary gas chromatography has already been the subject of several studies. Hively and Hinton¹ published retention indices and their temperature increments for C₂-C₇ *n*-alkynes on squalane. Meltzow *et al.*² separated *n*-hexyne isomers on a capillary column with Arneel SD as a polar stationary phase. The separation and characterization of C₆-C₁₄ *n*-alkyne isomers were studied by Rang and co-workers³⁻⁷ on columns with phases of various polarities: squalane, Apiezon L, polyphenyl ether, PEG 4000, Carbowax 20M and 1,2,3-tris(2-cyanoethoxy)propane. Dielmann⁸ studied the retention behaviour of some linear C₅-C₂₀ *n*-alkynes on silicone oil DC 200 and polypropylene glycol (PPG) stationary phase.

The above studies demonstrated that the separation of *n*-alkyne isomers up to C₉ on both non-polar and polar stationary phases is not difficult. However, as the number of carbon atoms increases, the demands on the separation of *n*-alkyne isomers, especially those with a central position of the triple bond, increase markedly. In the range up to C₁₄, 5- and 4-decynes, -undecynes, and -dodecynes, 6- and 5-

dodecynes and -tridecynes and 7- and 6-tetradecynes are the most difficult to separate pairs. On all of the stationary phases considered, only partial separations of these critical pairs of isomers were obtained, although high-efficiency capillary columns were used.

As shown by an example of the separation of *n*-alkene isomers^{9,10}, similar separation problems can be solved by using separation systems combining high efficiency with high selectivity, *i.e.*, on liquid crystals as stationary phases coated in capillary columns. We therefore investigated the possibility of using liquid crystals for the separation of C₆-C₁₄ *n*-alkyne isomers. Considering the significance of squalane as the stationary phase for the characterization of hydrocarbons and the significant differences in the retention data published for *n*-alkynes, we checked the reproducibility of retention indices on this stationary phase in capillary gas chromatography. From retention indices measured for *n*-alkyne isomers, structure-retention correlations, important from the viewpoint of characterization, were derived such as increment due to the methylene group (I_{CH_2}), homomorphous factor (H) and temperature increment of the retention index (dI/dT). These structure-retention correlations were also studied on a liquid crystal as the stationary phase, particularly from the viewpoint of the role of fine structural features of the zig-zag arrangement of the carbon chain of *n*-alkynes (alternations of the retention) and the propyl group attached to the carbon atom bearing a triple bond.

EXPERIMENTAL

Model mixtures, including all positional isomers of C₆-C₁₄ *n*-alkynes, composed of individual reference materials¹¹, were used. A Perkin-Elmer F-11 gas chromatograph with a flame-ionization detector was used to measure the retention characteristics of *n*-alkyne isomers. The temperature in the thermostat was measured with a precision of $\pm 0.1^\circ\text{C}$. Hydrogen served as the carrier gas. *n*-Alkynes were separated on high-efficiency glass capillary columns coated with squalane and 4-*n*-pentylacetophenone-(*O*-4-*n*-pentyloxybenzoyloxime) (PBO) nematic liquid crystal⁹ having the mesophase in the range 63-94°C (undercoolable to 27°C).

Capillaries of soda-lime glass, Unihost type (Kavalier, Teplice, Czechoslovakia), drawn with a drawing equipment of our own design, were used for the preparation of the columns. Capillaries of I.D. 0.25 mm were drawn with a precision of $\pm 3\%$. The internal surface of the capillaries was roughened by etching with gaseous hydrogen chloride¹². The capillaries used for the preparation of columns with squalane were deactivated, prior to coating, by silanization in the gaseous phase with hexamethyldisilazane-trimethylchlorosilane (5:1) at 220°C for 20 h. Capillaries were coated by the dynamic method with a 10-30% solution of squalane in *n*-hexane and with a 1.5-15% solution of PBO in chloroform at a speed of $1\text{ cm} \cdot \text{s}^{-1}$. The squalane used was obtained from three different sources (E. Merck, Darmstadt, F.R.G., May & Baker, Dagenham, U.K., and BDH, Poole, U.K.). The PBO liquid crystal was synthesized at the Martin Luther University in Halle-Wittenberg, G.D.R.⁹. The squalane film thickness was determined from its mass in the column and also from the capacity ratio of *n*-octane¹³ at 80°C (with an agreement of 0.05 μm).

Samples were introduced into the column with the aid of a splitter with 1:100 splitting ratio so that the sample size ranged from 10^{-9} to 10^{-10} g per component.

Retention times were measured from the methane peak. The repeatability of the measurements of retention indices expressed in terms of the standard deviation of the arithmetic mean was ± 0.03 i.u. on squalane and ± 0.05 i.u. on PBO. Table I gives the characteristics of the capillary columns used.

RESULTS AND DISCUSSION

Squalane as the stationary phase

Reproducibility of retention indices. In gas-liquid chromatography, reproducible retention indices can be obtained by using separation systems in which the contribution of adsorption plays a negligible role¹⁴. In the separation of hydrocarbons, this condition is fulfilled by separation systems with non-polar stationary phases in columns with the lowest possible adsorption activity of the support (walls of the capillary column). The effect of ageing of the stationary phase on the retention indices is also of lesser significance in such systems. For these reasons we used squalane as the stationary phase and glass capillary columns in characterizing *n*-alkyne isomers. Systematic differences in the range 1.7–3.3 i.u. are obvious from a comparison of published retention indices of *n*-alkynes on squalane^{1,3}. Schomburg¹⁵ found a difference of 4.9 i.u. between the retention indices of 3-octyne on a glass and a stainless-steel capillary column coated with squalane. When measuring the retention indices of *n*-alkynes, we therefore studied the effects of squalane quality, the procedure for the preparation of the column surface, the thickness of the squalane film and the type and the pressure of the carrier gas.

Because of the poor reproducibility of the retention indices of *n*-alkynes, we also used other types of hydrocarbons (*o*-xylene, benzene, cyclohexane) to characterize the separation systems. Fig. 1 shows the dependence of the retention indices

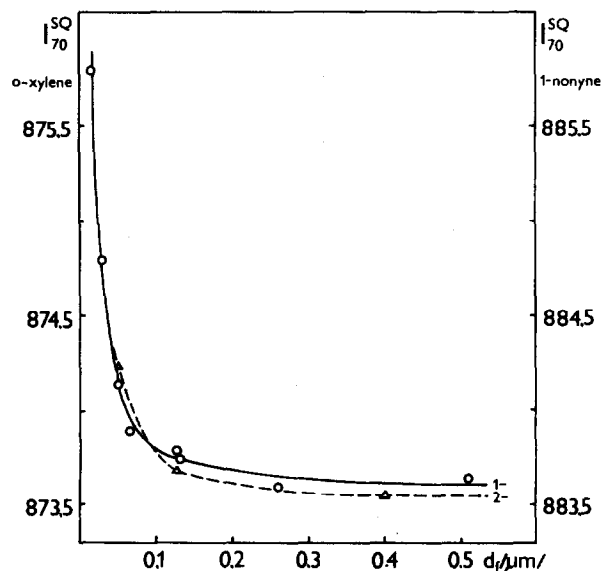


Fig. 1. Dependence of the retention indices of *o*-xylene (1) and 1-nonyne (2) at 70°C on the film thickness, d_f , of squalane on a glass capillary column roughened with gaseous hydrogen chloride.

TABLE I
PARAMETERS OF GLASS CAPILLARY COLUMNS (I.D. 0.25 mm) COATED WITH SQUALANE AND PBO, MEASURED AT 80°C

Parameter	Squalane							PBO						
	1	2	3	4	5	6	7	1	2	3	4	5	6	7
Length (m)	107	106	52	102	90	110	62							
Average film thickness of squalane (μm)	0.40	0.12	0.10	—	—	—	—							
H ₂ carrier gas inlet pressure (MPa)	0.26	0.26	0.18	0.25	0.18	0.25	0.14							
Linear H ₂ carrier gas flow-rate ($\text{cm} \cdot \text{sec}^{-1}$)	36	36	55	36	38	34	36							
Theoretical plate number, <i>N</i>	359,500	318,600	145,300	113,500	273,700	400,000	137,600							
Effective plate number, <i>n</i>	256,800	274,500	125,000	80,000	221,800	270,000	104,000							
Capacity ratio, <i>k</i>	5.4	12.5	12.6	5.1	9.0	4.6	6.6							
Separated <i>n</i> -alkynes (<i>n</i> C)	C ₆ -C ₈	C ₉ -C ₁₁	C ₁₂ -C ₁₄	C ₆ -C ₉	C ₁₀ -C ₁₄	C ₁₀ -C ₁₄	C ₁₂ -C ₁₄							
Retention index of 1-nonyne	883.15	883.17	883.23	980.2	980.0	980.3	980.7							
Capacity ratio of 1-nonyne	—	—	—	2.8	0.5	0.5	0.2							

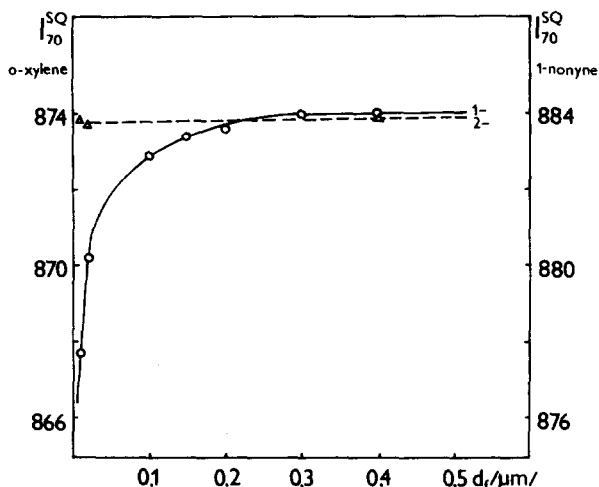


Fig. 2. Dependence of the retention indices of *o*-xylene (1) and 1-nonyne (2) at 70°C on the film thickness, d_f , of squalane on a glass capillary column with a smooth internal surface.

of 1-nonyne and *o*-xylene on the thickness of the squalane film at 70°C in glass capillaries with the surface roughened by etching with gaseous hydrogen chloride. It can be seen that on such columns, with a squalane film thinner than 0.1 μm the retention indices of both compounds increase as the film thickness decreases, obviously as a result of adsorption on the phase interface. In columns with a squalane film thicker than 0.1 μm , both retention indices are virtually independent of the film thickness.

In squalane columns prepared by coating glass capillaries with a smooth and unsilanized internal surface (they have low efficiency and a short service life), with a film thickness greater than 0.2 μm the retention index of *o*-xylene does virtually not change (Fig. 2). In columns with a thinner squalane film, in contrast to the dependence in Fig. 1, however, a marked decrease in the retention indices of *o*-xylene and also benzene ($I_{30}^{\text{SQ}} = 626.0$) and cyclohexane ($I_{30}^{\text{SQ}} = 652.6$) was observed, whereas the retention index of 1-nonyne on these columns with a squalane film thickness in the range of 0.01–0.4 μm did not change. It can also be seen from Figs. 1 and 2 that with the squalane films thicker than 0.2 μm , the retention index of 1-nonyne (and also that of *o*-xylene) is 0.3 i.u. greater in a column with an unroughened surface.

TABLE II

RETENTION INDICES OF 1-NONYNE AND *o*-XYLENE AT 70°C ON SQUALANE COLUMNS

Column, 50 m \times 0.25 mm I.D.; carrier gas, hydrogen, 0.12 MPa.

Compound	Source of squalane I_{70}^{SQ}		
	Merck	May & Baker	BDH
1-Nonyne	883.2	883.5	884.1
<i>o</i> -Xylene	873.5	873.7	875.0

TABLE III

RETENTION INDICES OF *n*-OCTYNES, 1-NONYNE, BENZENE, CYCLOHEXANE AND *o*-XYLENE ON MAY & BAKER SQUALANE AT 70°C

Compound	k''			ΔI	
	0.4 MPa H ₂	0.4 MPa N ₂	0.26 MPa H ₂	N ₂ - H ₂ (0.4 MPa)	H ₂ (0.4 - 0.26 MPa)
Benzene	641.51	641.96	641.45	0.45	0.06
Cyclohexane	667.14	667.46	667.02	0.32	0.12
1-Octyne	783.52	783.60	783.52	0.08	0.00
2-Octyne	843.45	843.60	843.46	0.15	-0.01
3-Octyne	819.28	819.37	819.29	0.09	0.01
4-Octyne	812.50	812.59	812.51	0.09	-0.01
<i>o</i> -Xylene	874.17	874.64	874.10	0.47	0.07
1-Nonyne	883.78	883.87	883.79	0.09	-0.01

The retention indices of 1-nonyne and *o*-xylene are also dependent on the type of the squalane used when the other conditions (film thickness, procedure for the preparation of the column wall and the type of carrier gas) are maintained constant. As can be seen from Table II, these differences range up to 1.5 i.u. and are obviously caused by the differences in the purity of commercially obtainable squalanes.

The influence of the type and pressure of the carrier gas on the retention indices of *n*-alkynes, *o*-xylene, benzene and cyclohexane was also investigated. As can be seen from Table III, when hydrogen was replaced with nitrogen as the carrier gas, the retention indices of *n*-alkynes were 0.1 i.u., those of *o*-xylene and benzene 0.45 i.u. and those of cyclohexane 0.3 i.u. higher for a nitrogen inlet pressure of 0.40 MPa. When the inlet pressure of hydrogen increased from 0.26 to 0.40 MPa, no change in the retention indices of *n*-alkynes was observed, whereas those of *o*-xylene and cyclohexane increased by 0.1 i.u. Hence the changes in the retention indices of *n*-alkynes caused by a change in the carrier gas and a change in its pressure are within the precision range of our measurements.

A significant increase in the retention indices of *n*-alkynes (and *o*-xylene) was observed on squalane columns owing to their natural ageing. For instance, on squalane on which the highest value of retention index of *o*-xylene was measured in columns with opened ends, this increase was about 0.5 i.u. per month.

All columns coated with squalane were prepared and tested on the basis of these results. When three columns with a squalane film thickness varying from 0.1 to 0.4 μm were used for C₆-C₁₄ *n*-alkyne isomers (*cf.*, Table I), a reproducibility of the retention indices in our laboratory in the region of 0.1 i.u. was obtained for *n*-alkynes, *o*-xylene, benzene and cyclohexane.

Table IV compares the retention indices of benzene, cyclohexane and *o*-xylene measured in our laboratory on glass and stainless-steel capillary columns with a film thickness of 0.3 μm with those reported by Rijks¹⁶, Rijks and Cramers¹⁷ and Schomburg in ref. 16. The retention indices from refs. 16 and 17 were converted for hydrogen as the carrier gas on the basis of the data from ref. 16. Lower retention indices of these hydrocarbons, measured in a glass capillary column, give evidence of the

TABLE IV

RETENTION INDICES OF BENZENE, CYCLOHEXANE AND *o*-XYLENE ON E. MERCK SQUALANE AT 70°C

1 = Glass capillary; 2 = stainless-steel capillary; 3 = in refs. 16 and 17; 4 = in ref. 16.

Compound	$I_{\%}^{\text{SQ}}$				ΔI_{1-2}	ΔI_{1-3}	ΔI_{1-4}
	1	2	3	4			
Benzene	640.8	642.2	641.5	641.7	-1.4	-0.7	-0.9
Cyclohexane	666.8	666.8	666.9	666.9	0.0	-0.1	-0.1
<i>o</i> -Xylene	873.5	874.9	875.0	874.2	-1.4	-1.5	-0.7

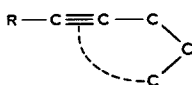
high purity of the squalane used and of the low adsorption activity of the wall of the capillary column. The results obtained suggest the possibility of a reproducibility of the retention indices of *n*-alkynes (and also of other hydrocarbons) on squalane of 0.1 i.u., provided that the separation system is defined by the thickness of the stationary phase film, internal column surface, type and pressure of the carrier gas or sorbent ageing. The retention indices of C_6 - C_{14} *n*-alkyne isomers measured on squalane at 80°C are presented in Table V.

Structure and retention behaviour of n-alkyne isomers. Increments due to the methylene group ($I_{\text{CH}_2}^{\text{SQ}}$), homomorphous factors (H^{SQ}) and temperature increments (dI/dT) were calculated from the measured retention indices of C_6 - C_{14} *n*-alkynes.

The values of $I_{\text{CH}_2}^{\text{SQ}}$ for C_6 - C_{14} *n*-alkyne isomers range from 94.0 to 102.8 i.u. and depend on the number of carbon atoms and the position of the triple bond in the molecule (Fig. 3). The increment due to the methylene group of *n*-alkyne homologues with identical positions of the triple bond increases as the carbon chain lengthens, and approaches 100. With a shift of the triple bond towards the centre of the molecule, this value is obtained for *n*-alkynes with longer carbon chains. Value of $I_{\text{CH}_2}^{\text{SQ}}$ higher than 100 were found for structures in which a propyl effect¹⁸ could be expected.

The dependence of H^{SQ} values on the number of carbon atoms for C_2 - C_{14} *n*-alkynes is shown in Fig. 4. The measured values were supplemented with the values published by Hively and Hinton¹ (adjusted to the difference in the polarities of the separation systems) for C_2 - C_5 *n*-alkynes.

The observed deviations from the regularities of the dependences of both $I_{\text{CH}_2}^{\text{SQ}} = f(C_n)$ and $H^{\text{SQ}} = f(C_n)$, systematically in the direction towards lower retentions, for 1-pentyne, 2-hexyne, 3-heptyne, 4-octyne and higher 4-alkynes are caused by the propyl effect¹⁸, which is an intermolecular ring interaction between the hydrogen atom of the terminal methyl moiety of the propyl group and the system of π -electrons, giving rise to a weakened interaction between the molecules of the solute and the solvent:



Based on the interpolation of the dependence $H^{\text{SQ}} = f(C_n)$, the contribution of the propyl effect to the retention index on squalane was determined, expressed in

TABLE V

RETENTION INDICES AND THEIR TEMPERATURE INCREMENTS FOR C₆-C₁₄ *n*-ALKYNES ON SQUALANE AND PBO AT 80°C USING HYDROGEN AS CARRIER GAS

<i>n</i> -Alkyne	I_{80}^{SQ}	$10 \cdot dI^{\text{SQ}}/dT^*$	I_{80}^{PBO}	dI^{PBO}/dT^*
1-Hexyne	583.4	0.13	678.0	0.08
2-Hexyne	640.3	-0.42	718.9	0.05
3-Hexyne	623.1	-0.85	692.8	0.05
1-Heptyne	683.6	0.12	779.1	0.06
2-Heptyne	743.0	-0.34	820.4	0.16
3-Heptyne	717.3	-0.69	782.4	0.09
1-Octyne	783.0	0.16	879.4	0.06
2-Octyne	842.3	-0.35	920.7	0.18
3-Octyne	818.0	-0.60	880.5	0.17
4-Octyne	811.3	-0.46	872.1	0.14
1-Nonyne	883.3	0.17	980.0	0.08
2-Nonyne	941.0	-0.32	1020.2	0.20
3-Nonyne	916.0	-0.60	980.0	0.18
4-Nonyne	910.4	-0.36	968.8	0.20
1-Decyne	983.2	0.17	1080.8	0.18
2-Decyne	1041.1	-0.30	1120.6	0.34
3-Decyne	1014.3	-0.49	1079.0	0.36
4-Decyne	1007.3	-0.30	1067.5	0.41
5-Decyne	1008.2	-0.23	1064.9	0.48
1-Undecyne	1083.3	0.15	1181.4	0.14
2-Undecyne	1140.9	-0.24	1220.7	0.35
3-Undecyne	1113.5	-0.44	1178.3	0.44
4-Undecyne	1104.8	-0.18	1164.7	0.48
5-Undecyne	1104.2	-0.14	1161.5	0.53
1-Dodecyne	1183.3	0.17	1282.2	0.15
2-Dodecyne	1240.8	-0.29	1321.0	0.36
3-Dodecyne	1212.5	-0.45	1277.6	0.44
4-Dodecyne	1203.3	-0.25	1263.1	0.50
5-Dodecyne	1201.1	-0.22	1258.2	0.58
6-Dodecyne	1199.6	0.00	1258.2	0.58
1-Tridecyne	1283.4	0.17	1382.9	0.15
2-Tridecyne	1340.6	-0.23	1421.2	0.38
3-Tridecyne	1311.9	-0.41	1377.1	0.44
4-Tridecyne	1301.5	-0.12	1361.6	0.53
5-Tridecyne	1298.5	0.13	1355.8	0.62
6-Tridecyne	1295.6	0.09	1353.4	0.64
1-Tetradecyne	1383.5	0.17	1483.4	0.14
2-Tetradecyne	1440.6	-0.27	1521.6	0.36
3-Tetradecyne	1411.1	-0.37	1476.6	0.46
4-Tetradecyne	1400.4	-0.26	1460.6	0.55
5-Tetradecyne	1396.4	0.11	1453.7	0.65
6-Tetradecyne	1392.5	0.19	1450.3	0.67
7-Tetradecyne	1390.5	0.28	1447.8	0.71

* dI^{PBO}/dT values of C₆-C₉ *n*-alkynes were measured in the temperature range 65-70°C and those of C₁₀-C₁₄ *n*-alkynes at 80-90°C; dI^{SQ}/dT values of C₆-C₉ *n*-alkynes were measured at 60-80°C, those of C₁₀-C₁₁ *n*-alkynes at 70-80°C and those of C₁₂-C₁₄ *n*-alkynes in the interval 90-100°C.

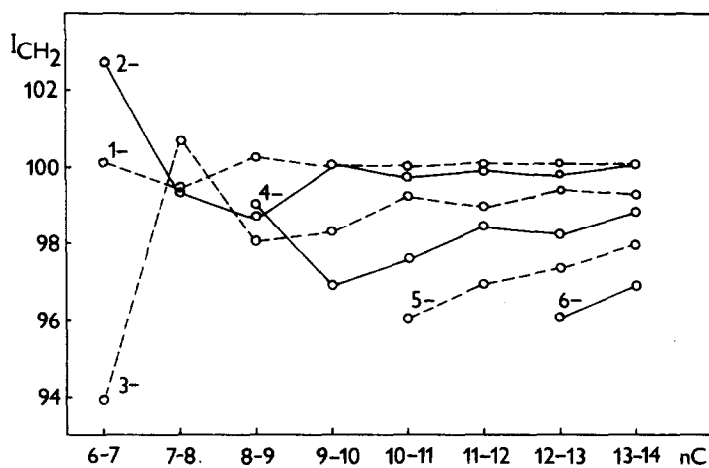


Fig. 3. Dependence of $I_{CH_2}^{80}$ on carbon number and on the position of the triple bond in the *n*-alkyne molecule on squalane at 80°C.

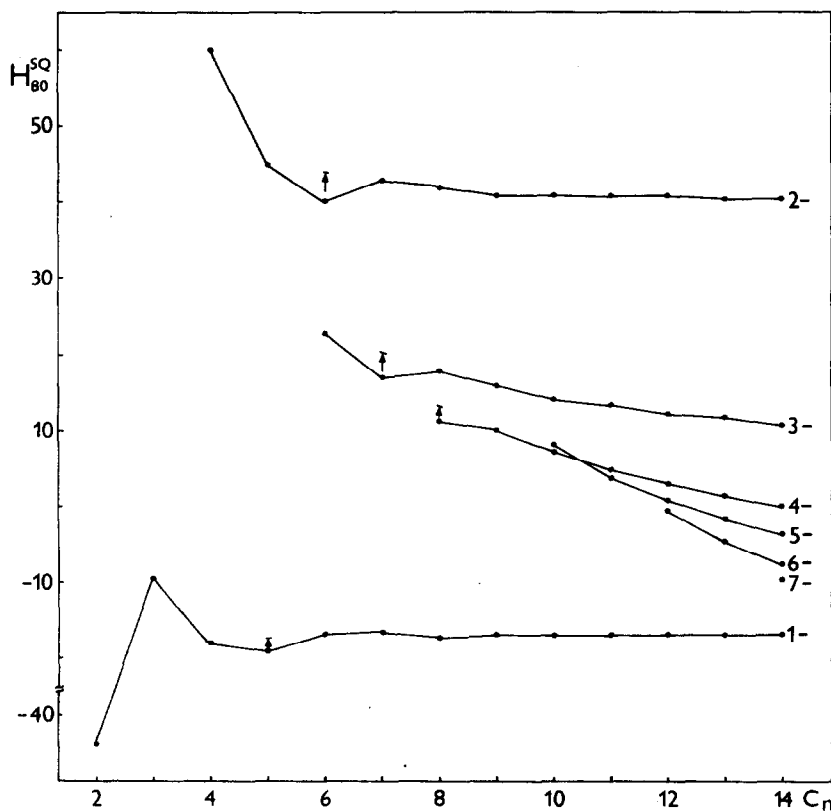


Fig. 4. Dependence of H_{80}^{80} on carbon number for homologous series of *n*-alkynes on squalane at 80°C. 1 = 1-Alkyne; 2 = 2-alkyne; etc.

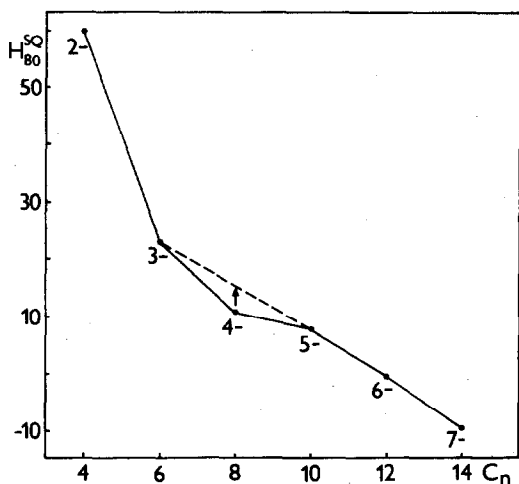
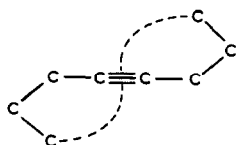


Fig. 5. Dependence of H_{80}^{SQ} on carbon number for the first members of n -alkyne homologous series.

terms of the difference between the measured and the interpolated values of the retention index of the particular n -alkyne. The values are 1.5, 3.7 and 3.0 i.u. for 1-pentyne, 2-hexyne and 3-heptyne, respectively. The contribution of the propyl effect for 4-octyne was determined on the basis of the dependence of H^{SQ} on the number of carbon atoms for the first members of the homologous series with a new structural feature (Fig. 5). The value found of 4 i.u. corresponds to a doubled contribution of the propyl effect found on the basis of dependence $H^{SQ} = f(C_n)$ for the homologous series of other 4-alkynes. This is in accord with the assumption that a double propyl effect applies with 4-octyne, similarly to *trans*-4-octene¹⁸:



As can be seen from Figs. 3 and 4, the above quantification of the influence of the propyl effect is, to a certain extent, also affected by the influence of retention alternation, which will be discussed later.

In a previous paper⁴, some characteristic dependences were found between the values of dI/dT on squalane and the structure of n -alkyne isomers up to C_{12} . In spite of this, in some instances, Dielmann⁹ did not confirm these trends by measurements on DC 200 and PPG because the dI/dT values are small. Our more precise measurements were used to investigate these relationships for n -alkynes up to C_{14} . As can be seen from Table VI, the values of $10 dI/dT$ on squalane for C_6 - C_{14} n -alkynes vary in the range 0.28 to -0.85 i.u., depending on the position of the triple bond and the length of the carbon chain. The dI/dT values are positive for all 1-alkynes and internal positional isomers starting from the 5-positional ones for tridecyne, *i.e.*, 5- and 6-tridecyne and 5-, 6- and 7-tetradecyne. For all other isomers the dI/dT values are

TABLE VI

TEMPERATURE INCREMENTS OF RETENTION INDICES, $10 \cdot dI/dT$, OF C_6 - C_{14} *n*-ALKYNE ISOMERS ON SQUALANE

<i>n</i> -Alkyne	Triple bond position							Temperature range (°C)
	1-	2-	3-	4-	5-	6-	7-	
Hexyne	0.13	-0.42	-0.85	-	-	-	-	60-80
Heptyne	0.12	-0.34	-0.69	-	-	-	-	60-80
Octyne	0.16	-0.35	-0.60	-0.46	-	-	-	60-80
Nonyne	0.17	-0.32	-0.60	-0.36	-	-	-	60-80
Decyne	0.17	-0.30	-0.49	-0.30	-0.23	-	-	70-80
Undecyne	0.15	-0.24	-0.44	-0.18	-0.14	-	-	70-80
Dodecyne	0.17	-0.29	-0.45	-0.25	-0.22	0.00	-	90-100
Tridecyne	0.17	-0.23	-0.41	-0.12	0.13	0.09	-	90-100
Tetradecyne	0.17	-0.27	-0.37	-0.26	0.11	0.19	0.28	90-100

negative, the most negative being obtained for 3-alkynes. The trends of the dependence of the dI/dT values on structure, published in ref. 4, were thus both confirmed and made more precise.

Separation of n-alkynes. 1-Alkynes are generally eluted on squalane prior to the other isomers. The retention of *n*-alkyne isomers with an internal position of the triple bond generally increases with a shift of the triple bond from the centre of the carbon chain towards the 2-position; the relatively higher retention of 2-alkynes is associated with the application of the hyperconjugation effect of the methyl group with the triple bond. The retention of 4-decyne before 5-decyne, affected by the propyl effect, is an exception to this rule. As a result of the propyl effect, the other 4-alkynes also have relatively lower retentions and are therefore eluted closer to 5-alkynes, thereby disturbing the regular decrease in the δI values of the neighbouring positional isomers with a shift of the position of the triple bond towards the centre of the molecule, which is also reflected in their difficult separation. On polar stationary phases, 4-decyne is eluted only after 5-decyne as a consequence of specific interactions.

The pairs consisting of one isomer with a new structural feature, *i.e.*, 6- and 5-dodecynes, 7- and 6-tetradecynes, etc., are additional difficult to separate pairs of *n*-alkyne isomers, similarly to *n*-alkenes. Comparison of the values of δI for the neighbouring positional isomers on squalane and on Carbowax 20M (Table VII) shows that these are only slightly greater for the polar stationary phase. As with the polarity of the stationary phase, the range of retentions of *n*-alkanes also decreases, and the increase in the δI values of the neighbouring positional isomers will be reflected in their actual separations to a substantially lesser extent. Moreover, the polarity of *n*-alkyne isomers decreases with a shift of the triple bond towards the centre of the molecule, so their adsorption on the surface of the polar stationary phase increases and hence also their retention. The change in the polarity of the stationary phase therefore does not affect the separation of *n*-alkyne isomers substantially. This also is why we separated *n*-alkyne isomers on liquid crystals as the stationary phases, utilizing the differences in the geometry of the molecules.

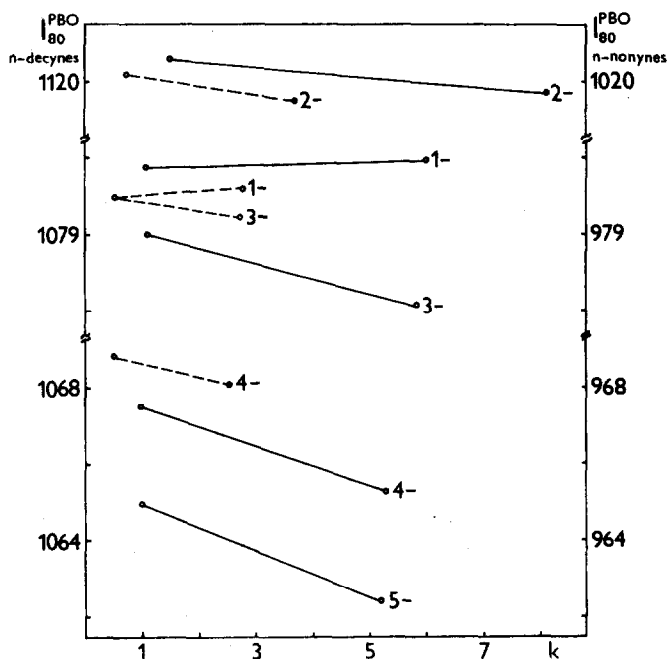


Fig. 6. Dependence of retention indices of isomers of *n*-nonynes (—) and *n*-decynes (---) on capacity ratio on PBO at 80°C.

Retention behaviour of n-alkyne isomers on 4-n-pentylacetophenone-(O-4-n-pentylxybenzoyloxime)

Reproducibility of retention indices. Measurements on PBO liquid crystal as the stationary phase were performed in the same temperature range as on squalane and on columns with varying film thickness. In general, liquid crystals are stationary phases of medium polarity and in the separation a mixed retention mechanism, dissolution and adsorption, occurs. The reproducibility of the retention indices of *n*-alkynes is therefore also worse than on squalane. For instance, the retention indices of *n*-nonynes and *n*-decynes differed systematically by -0.2 to $+2.5$ i.u. on two columns (Nos. 4 and 5 in Table I) with varying film thickness of PBO, depending on the number of carbon atoms in the chain and on the position of the triple bond (Fig. 6). The slope of the dependence $I = f(k)$ increases with a shift of the triple bond towards the centre of the *n*-alkyne molecule as its polarity decreases in this direction and the adsorption of *n*-alkyne isomers on the surface of the polar stationary phase increases.

On investigating the retention data of *n*-alkynes (net retention times, retention indices) and column efficiency during conditioning of the freshly prepared column with PBO liquid crystal at 90°C (in the range of the mesophase), we found that the retention characteristics increase up to virtually constant values. The changes in the retention indices of *n*-alkyne isomers depend on the position of the triple bond in the carbon chain, so that the greatest increase in the retention indices is observed for internal positional *n*-alkynes and the lowest for 1-alkynes. For instance, for *n*-un-

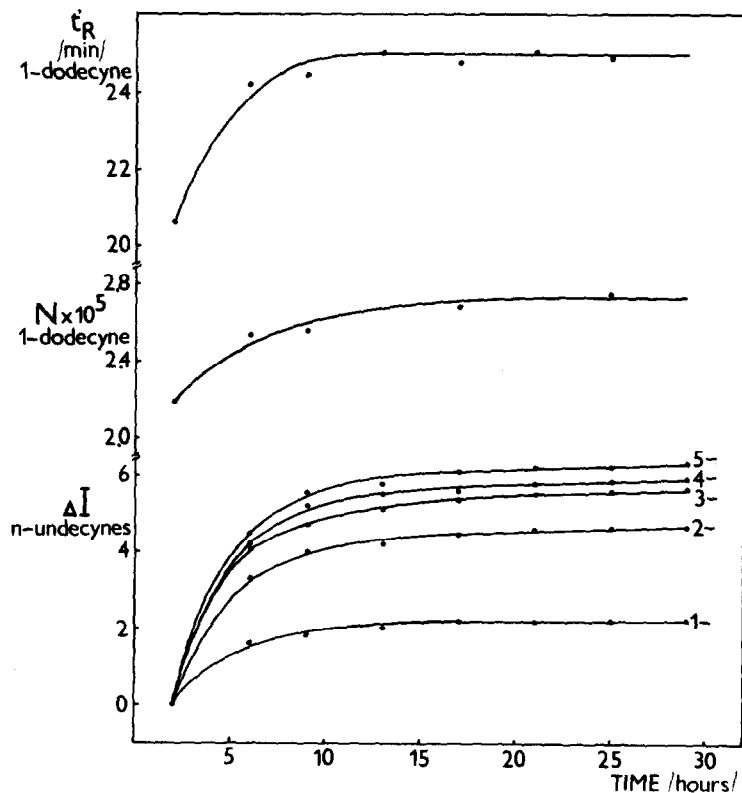


Fig. 7. Dependence of retention time of 1-dodecyne, column efficiency and retention indices of *n*-undecynes on the time of conditioning of the freshly prepared column with PBO at 90°C.

decynes it is from 2 i.u. for 1-undecyne to 6.5 i.u. for 5-undecyne (Fig. 7). This is obviously associated with the changes in the macrostructure of the liquid crystal on the surface of the column (orientation of liquid crystal molecules towards the column surface) and thus also with the change in its selectivity caused by the change in adsorptive properties. In view of this dependence, we measured the retention indices of the C_6 - C_{14} *n*-alkynes in the range of insignificant changes in retention indices with

TABLE VII

VALUES OF δI FOR NEIGHBOURING POSITIONAL ISOMERS OF C_{12} - C_{14} 5- AND 6- AND 6- AND 7-*n*-ALKYNES ON SQUALANE AND CARBOWAX 20M AT 110°C

<i>n</i> -Alkyne	δI^{SQ}		δI^{CW}	
	5-/6-	6-/7-	5-/6-	6-/7-
<i>n</i> -Dodecyne	0.5	—	1.8	—
<i>n</i> -Tridecyne	3.0	—	3.4	—
<i>n</i> -Tetradecyne	3.5	1.2	4.6	1.2

TABLE VIII
 VALUES OF α FOR NEIGHBOURING POSITIONAL ISOMERS OF C₁₀-C₁₄ *n*-ALKYNES ON SQUALANE AND PBO AT 80 AND 90°C

<i>n</i> -Alkyne	α_{80}^{S0}				α_{80}^{PBO}				α_{90}^{PBO}						
	Decyne	Undecyne	Dodecyne	Tridecyne	Tetradecyne	Decyne	Undecyne	Dodecyne	Tridecyne	Tetradecyne	Decyne	Undecyne	Dodecyne	Tridecyne	Tetradecyne
2-/1-	1.609	1.602	1.553	1.551	1.545	1.355	1.347	1.341	1.337	1.336	1.341	1.347	1.341	1.337	1.336
2-/3-	1.246	1.250	1.245	1.250	1.253	1.374	1.379	1.359	1.365	1.371	1.374	1.379	1.359	1.365	1.371
3-/4-	1.059	1.074	1.073	1.081	1.083	1.092	1.109	1.105	1.111	1.114	1.092	1.109	1.105	1.111	1.114
4-/5-	0.993	1.005	1.018	1.022	1.031	1.020	1.025	1.031	1.035	1.044	1.020	1.025	1.031	1.035	1.044
5-/6-	—	—	1.008	1.023	1.031	—	—	1.000	1.017	1.024	—	—	1.000	1.017	1.024
6-/7-	—	—	—	—	1.014	—	—	—	—	1.015	—	—	—	—	1.015

TABLE IX

VALUES OF α FOR NEIGHBOURING HOMOLOGUES OF *n*-ALKANES AT 70°C ON COLUMNS 4, 5 AND 7 (SEE TABLE I) WITH VARYING THICKNESS OF PBO FILM

Column No.	α_{70}^{PBO}		
	nC_9/nC_8	nC_{10}/nC_9	nC_{11}/nC_{10}
4	2.2605	2.2542	—
5	2.1979	2.2480	2.2398
7	—	—	2.1827

time (Table V). Better repeatability and reproducibility of the measurement of retention indices were then obtained.

Selectivity. Table VIII gives the retention ratios, α , for neighbouring positional isomers of C_{10} – C_{14} *n*-alkynes on squalane and PBO liquid crystal. It can be seen that the values of α are, in general, considerably greater for the liquid crystal, which suggests that the selectivity of the liquid crystal for *n*-alkynes increases with a shift of the triple bond from the centre towards the end of the carbon chain. This is also confirmed by the α values for 2- and 1-alkyne pairs, which are lower on the liquid crystal than on squalane as a consequence of the higher selectivity of the liquid crystal for 1-alkynes. As will be shown further, the exception found for 5- and 6-alkyne pairs is associated with alternation of retention on the liquid crystal. Similar dependences between the selectivity and the position of the multiple bond were also observed for *n*-alkenes¹⁰.

Table IX compares the values of α for *n*-alkanes in columns with varying film thickness of the liquid crystal. The values of α measured on the column with a thinner film are lower, which suggests a decrease in the liquid crystal selectivity. As the film thickness of PBO decreases, the contribution to the retention of *n*-alkane adsorption on the liquid crystal surface becomes relatively greater, which acts against the above mentioned effect. As the values of α for *n*-alkanes decrease as the film thickness decreases, it suggests that the influence of the change in selectivity is more marked than that of the change in the contribution of the adsorption in the separation system.

Alternation of retention. Published physico-chemical characteristics, such as boiling points, melting points, specific gravity and refractive indices of *n*-alkynes¹⁹, show a certain alternation of these quantities with carbon atom number and with the position of the triple bond. *n*-Alkynes with an even number of carbon atoms in the chain and with an even-carbon position of the triple bond or *n*-alkynes with an odd number of carbon atoms in the chain and with odd-carbon position of the triple bond give higher values. 2-Alkynes, in comparison with the other isomers, show the maximum value of a given quantity as a consequence of hyperconjugation effect. As is obvious from the dependence of the retention ratios of the neighbouring homologues of *n*-alkynes, $\alpha^{SQ} = f(C_n)$ (Fig. 8) and $\alpha^{PBO} = f(C_n)$ (Fig. 9), alternation also applies to the retention of *n*-alkynes on squalane and on the liquid crystal. 1-Alkynes with an even number of carbon atoms, 3-alkynes with an odd number of carbon atoms, etc., show relatively higher retentions.

Vigdergauz and Seomkin²⁰ reported the alternation of the retentions of *n*-alkanes on PEG 400 polar stationary phase when they found higher retentions of

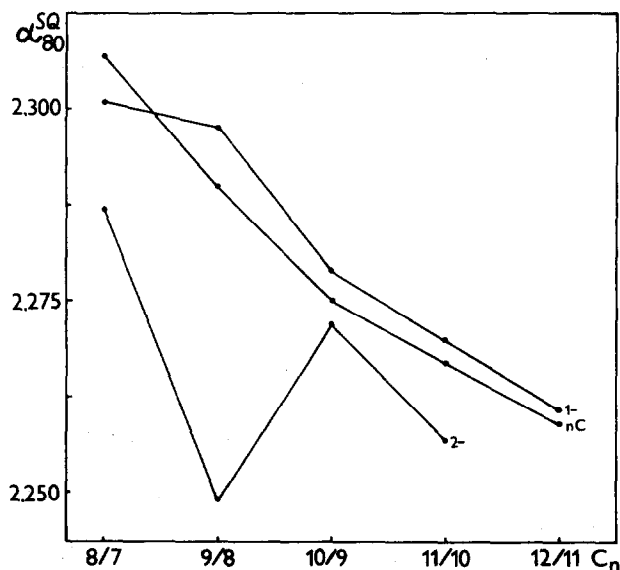


Fig. 8. Dependence of α on the number of carbon atoms for neighbouring members of *n*-alkyne and *n*-alkane homologous series on squalane at 80°C. 1 = 1-Alkyne; 2 = 2-alkyne; nC = *n*-alkane.

n-alkanes with an even number of carbon atoms in the chain. We did not observe an alternation of the *n*-alkane retentions on either squalane or PBO. On the other hand, the retentions of *n*-alkyne isomers show a significant alternation depending on the position of the triple bond and on the number of carbon atoms in the chain. From a comparison of Figs. 8 and 9 and from the decrease in the retention alternation with

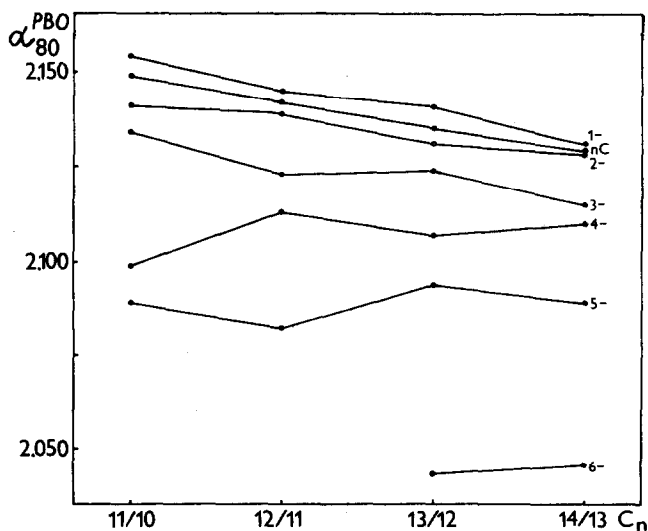


Fig. 9. Dependence of α on the number of carbon atoms for neighbouring members of *n*-alkyne homologous series on PBO at 80°C. 1 = 1-Alkyne; 2 = 2-alkyne; etc.; nC = *n*-alkane.

increasing length of the carbon chain, it follows that the alternation of the retentions of *n*-alkynes on the liquid crystal is greater than on squalane as a consequence of the higher selectivity of the liquid crystal towards changes in molecule geometry. It can also be seen from Fig. 9 that with a shift of triple bond towards the centre of the chain, the amplitude of the retention alternation also increases. This is associated with the fact that the selectivity of the liquid crystal is generally connected with steric restriction of the mobility of solute molecules. With *n*-alkynes, the properties of their isomers become more similar with a shift of the triple bond towards the centre of the carbon chain and therefore the contribution of the zig-zag arrangement to the geometry of the carbon chain, being responsible for the alternations, is relatively higher.

Separation of n-alkynes. As *n*-alkyne isomers with an internal position of triple bond are eluted on PBO liquid crystal in the same sequence as on common stationary phases, *i.e.*, in accord with the shift of the triple bond from the centre towards the end of the chain, and also their selectivity increases in the same direction, their separation is easier. As follows from a comparison of the dependences $H^{SQ} = f(C_n)$ and $H^{PBO} = f(C_n)$, the advantage of the use of the liquid crystal will be more marked for the separation of C_{10} and higher *n*-alkynes. Depending on the polarity of the stationary phase used, the retention of 1-alkynes changes from those of internal positional up to those of 2-positional *n*-alkynes. As liquid crystals are stationary phases

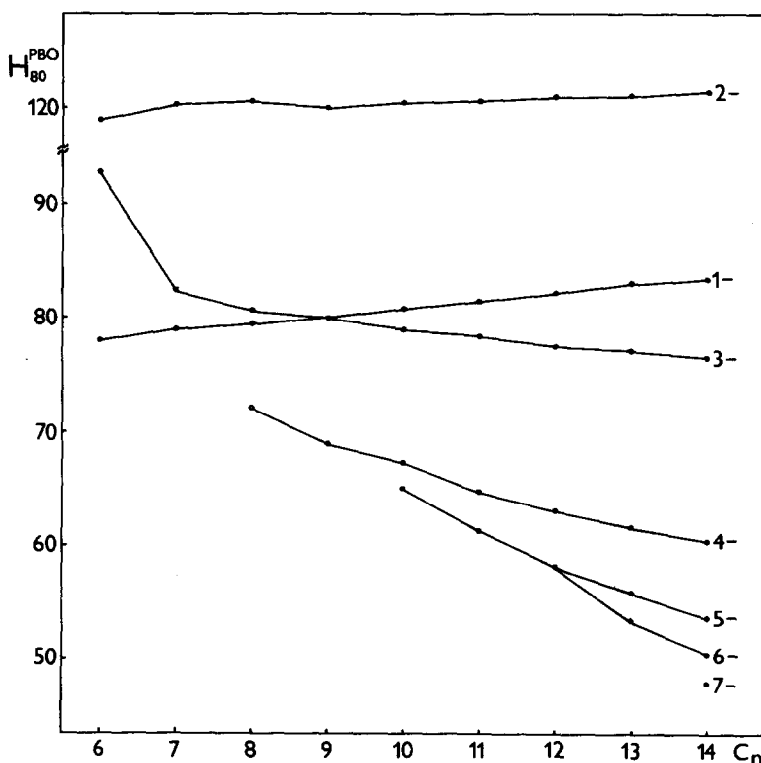


Fig. 10. Dependence of H_{80}^{PBO} on the number of carbon atoms for C_6 - C_{14} *n*-alkynes on PBO at 80°C. 1 = 1-Alkyne, etc.

of medium polarity, 1-alkynes are eluted in the vicinity of 3-alkynes. At the same time, 1-alkynes up to C_9 elute at 80°C prior to the corresponding 3-alkynes, whereas C_{10} and higher 1-alkynes elute in a reverse sequence (Fig. 10). Lower values of α for 5- and 6-*n*-alkyne pairs on PBO, if compared with squalane (Table VIII), and hence also poorer separations, are connected with the retention alternation effect owing to the change in the length of the carbon chain and to the position of the triple bond when, for instance, relatively more selectively retained 6-dodecyne (even number of carbon atoms in the chain and even-carbon position of the triple bond) is eluted together with 5-dodecyne. A reverse sequence of the elution of 4- and 5-decyne, compared with squalane, was obtained for the same reason. On squalane, as a consequence of the propyl effect, 4-decyne elutes anomalously prior to 5-decyne. 4-Decyne elutes after 5-decyne because the difference in the linearity of the two isomers applies on the liquid crystal as well as its polarity. Hence more complete and more rapid separations of *n*-decyne isomers and of other *n*-alkynes up to C_{14} , except for the 5- and 6- C_{12} - C_{14} pairs, are obtained on liquid crystals than on common stationary phases. The problem of the separation of 6- and 5-dodecyne can probably be solved on a still more selective liquid crystal so as to obtain elution of 6-dodecyne only after 5-dodecyne, as with *trans*-5- and 6-dodecenes¹⁰. The separation of C_{10} - C_{14} *n*-alkyne isomers on squalane and PBO liquid crystal is demonstrated in Figs. 11-15. Experimental conditions (film thickness of the stationary phase, flow-rate of the carrier

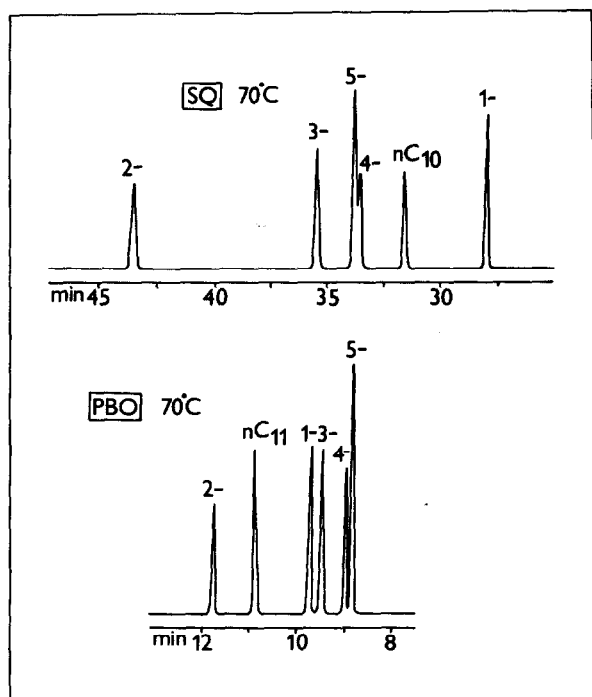


Fig. 11. Separation of *n*-decyne isomers on capillary columns with squalane (No. 2) and PBO (No. 5). 1 = 1-Decyne, etc.; nC_{10} = *n*-decane; nC_{11} = *n*-undecane.

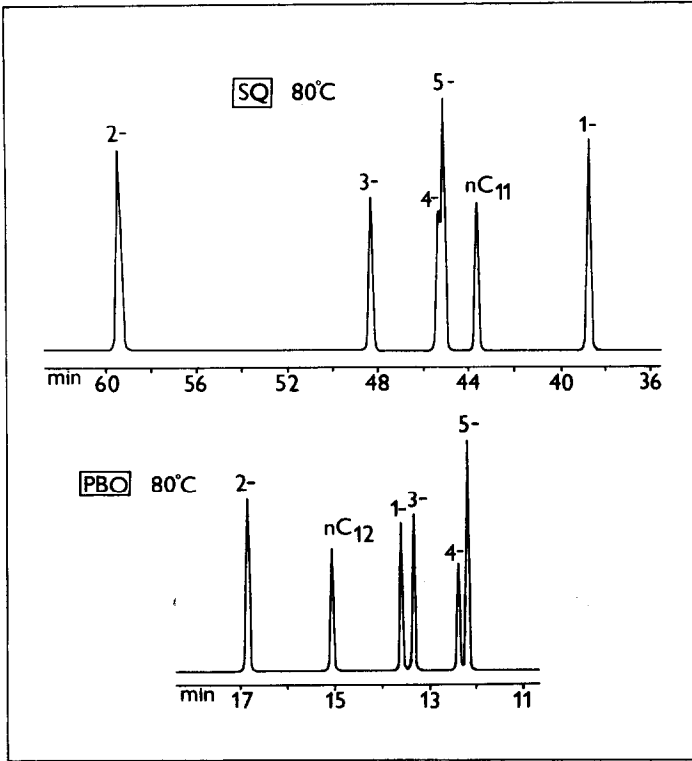


Fig. 12. Separation of *n*-undecyne isomers on capillary columns with squalane (No. 2) and PBO (No. 5). 1 = 1-Undecyne, etc.; nC₁₁ = *n*-undecane; nC₁₂ = *n*-dodecane.

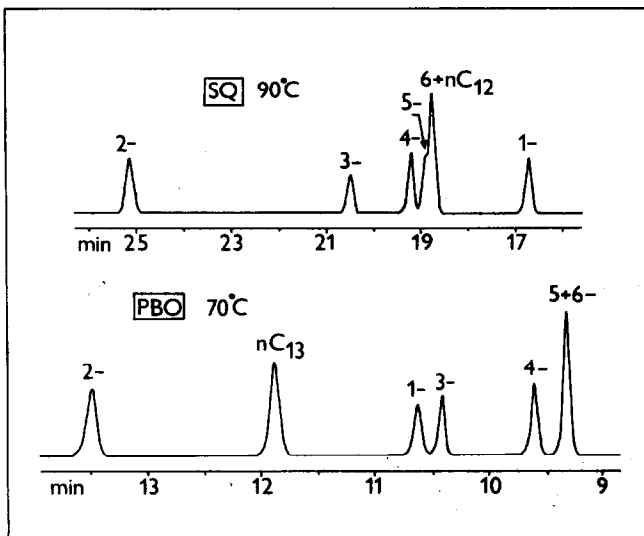


Fig. 13. Separation of *n*-dodecyne isomers on capillary column with squalane (No. 3) and PBO (No. 5). 1 = 1-Dodecyne, etc.; nC₁₂ = *n*-dodecane; nC₁₃ = *n*-tridecane.

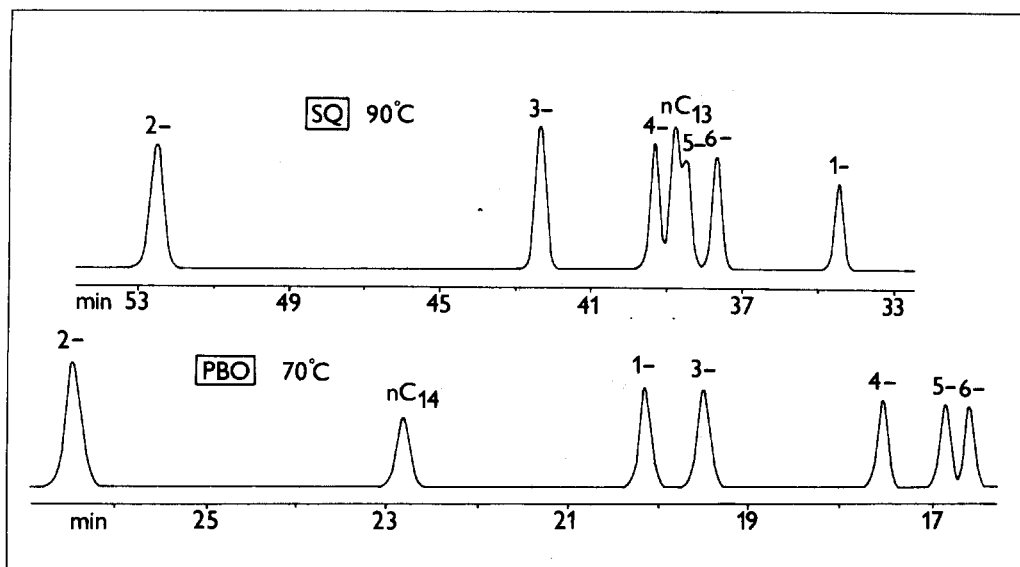


Fig. 14. Separation of *n*-tridecyne isomers on capillary columns with squalane (No. 3) and PBO (No. 7). 1 = 1-Tridecyne, etc.; nC_{13} = *n*-tridecane; nC_{14} = *n*-tetradecane.

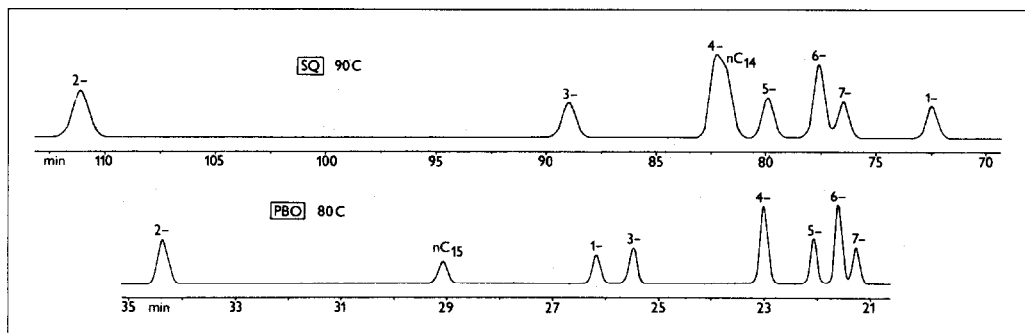


Fig. 15. Separation of *n*-tetradecyne isomers on capillary columns with squalane (No. 3) and PBO (No. 7). 1 = 1-Tetradecyne, etc.; nC_{14} = *n*-tetradecane; nC_{15} = *n*-pentadecane.

the carrier gas) were selected for the separation of those alkynes so as to obtain the optimum analysis time.

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