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CAPILLARY GAS CHROMATOGRAPHY OF *n*-ALKYNES

I. RETENTION INDICES

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SUMMARY

Retention indices (*I*) of C₆-C₁₄ *n*-alkynes have been determined on squalane, Apiezon L, polyphenyl ether and polyethylene glycol 4000 in the temperature range 60-190° and are correlated with the structure of the isomers. The effects on *I* of the position of the triple bond, of the chain-length and of the polarity of the liquid phase are discussed. Equations are presented which describe the linear dependences of *I* on the number of carbon atoms in the molecules, *n*. The best resolution of positional isomers has been obtained on squalane.

INTRODUCTION

During investigation of the relations between the gas chromatographic (GC) behaviour and molecular structure of unsaturated hydrocarbons, it was apparent that few retention data were available for *n*-alkynes up to C₉ (refs. 1-4), whereas higher isomers had not been examined at all. As the contribution of the triple bond to the retention is of considerable theoretical and practical interest, we have investigated more systematically the trends in the retention indices with the molecular structure of C₆-C₁₄ *n*-alkynes on four stationary liquid phases (squalane, Apiezon L, polyphenyl ether and polyethylene glycol 4000), which are often used in analytical practice. Because of their high molecular weights and high boiling points, tri- and tetradecynes could not be measured on squalane; however, the non-polar phase Apiezon L could be used for the analysis of these compounds.

EXPERIMENTAL

The alkynes were synthesized by alkylation of acetylene in liquid ammonia⁵ and were purified by use of preparative GC. Their purity was 95-99.9%, as determined by capillary GC. All measurements were made on capillary columns in order to achieve better separation of the positional isomers. Chrom-2 and Chrom-3 instruments were used with a flame ionization detector. The carrier gas was nitrogen, helium or hydrogen. Mixtures of *n*-alkynes and *n*-alkanes were employed in quantities,

that maintained the symmetry of the peaks at the maximum sensitivity. Variation of sample size within the range 0.01–0.05 mm³ had no effect on the retention times. The split ratio was *ca.* 1:200. Table I gives the working conditions and characteristics of the stainless-steel capillary columns which were coated by a dynamic method⁶.

TABLE I

EXPERIMENTAL CONDITIONS

	<i>Stationary phase</i>			
	<i>Squalane</i>	<i>Apiezon L</i>	<i>Polyphenyl ether</i>	<i>Polyethylene glycol 4000</i>
Column length* (m)	100	50	45	100
Column temperature (°C)	90–130	110–190	90–170	60–160
Column efficiency (number of theoretical plates for 2-decyne)	113 000	36 000	53 000	73 000
Pressure at inlet (kg/cm ²)	1.6–2.6	1.5–2.0	1.2–1.6	1.6–2.6
Carrier gas flow-rate (ml/min)	0.3–0.4	0.2–0.5	0.1–0.5	0.2–0.3

* Inner diameter, 0.25 mm.

Retention indices were calculated by means of Kováts formula⁷. The dead time was determined by the method described in ref. 6. The reproducibility of the measurements, calculated as the standard deviation of at least five measurements at each temperature, was ± 0.6 index units (i.u.) for C₆–C₁₀ and ± 0.4 i.u. for higher *n*-alkynes on squalane (SQ) and polyethylene glycol 4000 (PEG), and ± 1 and ± 0.8 i.u. on polyphenyl ether (PPE) and Apiezon L (ApL), respectively.

The constants of the equations $I = a + bn$, describing the linear dependences of *I* on *n*, were calculated with a computer by means of a least-squares method. The *I* values determined in this work for C₆–C₇ *n*-alkynes on squalane are in good agreement with the previous data of Hively and Hinton⁴.

RESULTS AND DISCUSSION

The elution order and the separation of positional isomers

The retention indices of *n*-alkynes are determined by their π -electron system and its polarization, and by steric factors due to the withdrawal of free rotation at the triple bond. The strength of the interaction between the slightly polar *n*-alkyne molecules and the molecules of the stationary liquid phase depends markedly on the polarity of the latter and increases in the order SQ < ApL < PPE < PEG. On SQ and ApL, where the main contribution to the intermolecular interaction is due to dispersion forces, the lowest *I* values were observed (Tables II–V). On polar PEG, dipole–dipole interactions resulted in the highest *I* values, *n*-alkynes with *n* carbon atoms were eluted near the *n*-alkane with (*n* + 2) carbon atoms (*e.g.*, *n*-decynes were eluted near *n*-dodecane).

The elution sequence and the resolution of positional isomers of C₁₀, C₁₂ and C₁₄ *n*-alkynes is shown in Fig. 1. On all of the stationary phases studied, the internal isomers with the same value of *n* were eluted in the order 7-, 6-, 5-, 4-, 3- and 2-alkynes,

TABLE II
RETENTION INDICES OF C₆-C₁₂ *n*-ALKYNES ON SQUALANE

Compound	Temperature (°C)					
	86*	90	100	110	120	130
1-Hexyne	586.7	584.0	584.0	583.9	583.7	583.7
2-Hexyne	642.2	640.3	639.4	638.4	638.3	638.5
3-Hexyne	624.3	622.8	621.5	619.9	619.6	618.9
1-Heptyne	686.3	684.3	684.4	684.2	684.5	684.4
2-Heptyne	744.5	743.2	742.7	742.0	741.6	741.3
3-Heptyne	718.1	717.1	716.3	715.8	715.0	714.3
1-Octyne		783.7	783.8	783.7	783.9	783.9
2-Octyne		842.4	842.0	841.4	840.9	840.5
3-Octyne		817.8	817.0	816.3	816.0	815.2
4-Octyne		811.3	810.7	810.3	809.7	809.2
1-Nonyne		883.9	884.1	884.1	884.4	884.5
2-Nonyne		941.2	940.8	940.6	940.2	939.7
3-Nonyne		915.8	915.1	914.7	914.0	913.3
4-Nonyne		910.5	910.1	909.7	909.2	908.7
1-Decyne		983.8	984.0	984.2	984.5	984.3
2-Decyne		1041.3	1041.0	1040.8	1040.4	1039.7
3-Decyne		1014.2	1013.8	1013.3	1012.8	1011.9
4-Decyne		1007.5	1007.3	1006.8	1006.5	1005.9
5-Decyne		1008.4	1008.1	1008.0	1007.7	1007.3
1-Undecyne				1084.2	1084.4	1084.5
2-Undecyne				1140.1	1140.1	1139.5
3-Undecyne				1112.4	1112.0	1110.8
4-Undecyne				1104.8	1104.4	1103.9
5-Undecyne				1104.3	1104.0	1103.7
1-Dodecyne				1184.4	1184.6	1184.4
2-Dodecyne				1239.8	1239.8	1239.1
3-Dodecyne				1211.4	1211.0	1210.1
4-Dodecyne				1203.3	1202.9	1202.4
5-Dodecyne				1201.7	1201.4	1201.3
6-Dodecyne				1200.3	1200.0	1200.2

* Ref. 1.

i.e., in agreement with the shift of the triple bond to the end of the molecule (only 4-decyne was eluted before 5-decyne on SQ and ApL).

On SQ and ApL this trend reflects the effect of changing the symmetry of the charge distribution in *n*-alkynes on dispersion interaction. On these liquid phases the elution sequence was nearly in accordance with the boiling points of the positional isomers, and 1-alkynes were eluted first.

1-Alkynes were retained more strongly on PEG due to the formation of hydrogen bonds, and emerged after all of the other positional isomers, except the 2-alkynes. The elution order of the internal alkynes is in accordance with the increase in the shielding effect of alkyl groups on the dipole-dipole interaction between the *n*-alkynes and the polar liquid phase as the triple bond shifts to the centre of the molecule. The magnitude of this effect increases markedly from methyl to *n*-propyl and, accordingly, the change in *I* values between the 2-, 3- and 4-isomers is more pronounced. The separation of internal alkynes in which the triple bond is situated more than four atoms away from the terminal carbon atom is more difficult

TABLE III
RETENTION INDICES OF C₁₀-C₁₄ *n*-ALKYNES ON APIEZON L

Compound	Temperature (°C)				
	110	130	150	170	190
1-Decyne	994.7	996.4	997.2		
2-Decyne	1051.9	1052.2	1050.6		
3-Decyne	1019.8	1019.3	1017.4		
4-Decyne	1012.3	1012.0	1010.8		
5-Decyne	1013.4	1013.3	1012.9		
1-Undecyne	1094.6	1095.5	1095.2	1096.1	
2-Undecyne	1151.4	1151.8	1150.8	1150.3	
3-Undecyne	1118.8	1118.6	1116.9	1116.1	
4-Undecyne	1110.5	1110.6	1109.9	1109.9	
5-Undecyne	1109.7	1110.1	1109.2	1109.1	
1-Dodecyne		1194.6	1195.2	1197.2	
2-Dodecyne		1251.0	1250.5	1250.4	
3-Dodecyne		1218.0	1216.4	1215.5	
4-Dodecyne		1208.4	1208.6	1208.5	
5-Dodecyne		1208.4	1207.4	1207.6	
6-Dodecyne		1206.6	1206.0	1206.4	
1-Tridecyne			1295.5	1297.2	1297.7
2-Tridecyne			1350.6	1351.0	1350.6
3-Tridecyne			1315.8	1315.0	1314.8
4-Tridecyne			1307.1	1306.9	1306.6
5-Tridecyne			1305.5	1305.7	1305.9
6-Tridecyne			1302.6	1303.5	1303.9
1-Tetradecyne			1395.7	1397.4	1398.3
2-Tetradecyne			1450.7	1451.2	1451.2
3-Tetradecyne			1414.9	1414.4	1414.5
4-Tetradecyne			1406.9	1406.5	1406.7
5-Tetradecyne			1403.9	1404.3	1405.1
6-Tetradecyne			1401.1	1401.2	1402.0
7-Tetradecyne			1400.2	1400.3	1400.7

as the shift of the triple bond towards the centre of the molecule leads to negligible variation in the symmetry and polarity of the molecule.

The difference, δI , between *I* values of neighbouring isomers depends on the polarity of the stationary phase. On a given phase and at a given temperature, the δI values decreased as the triple bond shifted towards the centre of the molecule (Table VI). The pairs of *n*-alkynes which possess the most distant positions of the triple bond from the terminal carbon atoms *e.g.*, 4- and 5-decyne, 5- and 6-dodecyne and 6- and 7-tetradecyynes, were the most difficult to separate. On PEG, where 1-alkynes were eluted after 3-alkynes, the maximum values of δI were found for 2- and 3-isomers. The separation of pairs of 1- and 2-alkynes depended slightly on the number of carbon atoms in each molecule; the resolution of pairs of 2- and 3-, 3- and 4-, 4- and 5- and 5- and 6-alkynes was improved as the carbon chain increased in length. The same trend has been observed⁸ with *n*-alkenes.

Using a capillary column of SQ, all of the isomers of the C₆-C₁₂ *n*-alkynes were separated except 4- and 5-undecyynes. On PEG, only 5- and 6-dodecyne were not separated.

TABLE IV
RETENTION INDICES OF C₃-C₁₄ *n*-ALKYNES ON POLYPHENYL ETHER

Compound	Temperature (°C)				
	90	110	130	150	170
1-Nonyne	1002.7	1003.4	1003.8		
2-Nonyne	1066.5	1067.6	1068.5		
3-Nonyne	1032.9	1032.5	1032.4		
4-Nonyne	1021.8	1022.0	1023.2		
1-Decyne	1102.7	1103.5	1104.3		
2-Decyne	1167.5	1169.0	1171.2		
3-Decyne	1131.8	1131.9	1132.0		
4-Decyne	1120.2	1121.0	1121.2		
5-Decyne	1120.6	1120.9	1121.5		
1-Undecyne	1201.5	1203.1	1204.5	1205.3	
2-Undecyne	1266.7	1267.6	1268.8	1269.6	
3-Undecyne	1230.0	1230.6	1231.2	1231.3	
4-Undecyne	1218.3	1219.0	1220.0	1221.2	
5-Undecyne	1217.9	1218.3	1219.2	1219.7	
1-Dodecyne		1302.9	1304.2	1304.7	
2-Dodecyne		1367.5	1368.4	1370.5	
3-Dodecyne		1329.4	1329.7	1330.1	
4-Dodecyne		1316.6	1317.6	1319.0	
5-Dodecyne		1315.8	1317.0	1317.6	
6-Dodecyne		1315.7	1316.6	1317.0	
1-Tridecyne		1402.6	1403.3	1404.7	1405.4
2-Tridecyne		1467.6	1468.2	1470.3	1471.1
3-Tridecyne		1429.2	1429.3	1429.4	1429.7
4-Tridecyne		1415.3	1416.4	1417.2	1417.3
5-Tridecyne		1414.0	1414.9	1415.5	1416.3
6-Tridecyne		1412.2	1413.7	1415.2	1416.1
1-Tetradecyne		1502.0	1503.1	1504.8	1505.8
2-Tetradecyne		1568.3	1569.1	1570.3	1570.9
3-Tetradecyne		1529.1	1529.2	1529.1	1529.1
4-Tetradecyne		1515.2	1516.0	1516.5	1517.2
5-Tetradecyne		1512.7	1512.9	1514.8	1514.9
6-Tetradecyne		1509.3	1511.1	1512.3	1513.5
7-Tetradecyne		1508.1	1509.3	1511.2	1512.3

Dependence of *I* on the number of carbon atoms

On all of the stationary phases studied, *I* exhibited a linear dependence on the number of carbon atoms in a molecule (Fig. 2). The constants *a* and *b* of the equations, $I = a + bn$, describing these linear relations are given in Table VII. The differences between the experimental and calculated values of the constants are less than 0.3%. The increments of *I* per CH₂ group (*I*_{CH₂}) were dependent on the number of carbon atoms in the molecule and on the position of the triple bond (Table VIII). As with *n*-alkenes⁸, lower *I*_{CH₂} values were found for the first members of the homologous series up to C₅-C₇ on SQ. For higher isomers, the *I*_{CH₂} values did not vary appreciably with *n*. Some of the alkynes, e.g., 1-pentyne, 2-hexyne and 3-heptyne, had markedly higher *I*_{CH₂} values on SQ, as observed with 1-pentene, *cis*- and *trans*-2-hexene and *trans*-3-heptene⁸. This anomaly in the behaviour of *n*-alkenes was explained in terms

TABLE V

RETENTION INDICES OF C₆-C₁₄ *n*-ALKYNES ON POLYETHYLENE GLYCOL 4000

I values for C₆-C₈ and C₁₂-C₁₄ *n*-alkynes at 110° were calculated from the dependences of *I* on column temperature⁹.

Compound	Temperature (°C)							
	60	80	100	110	120	140	150	160
1-Hexyne	836.8	832.8		827.1				
2-Hexyne	836.7	862.2		860.3				
3-Hexyne	831.5	829.0		825.2				
1-Heptyne	937.5	934.2		929.0				
2-Heptyne	964.9	964.4		964.8				
3-Heptyne	915.5	913.3		910.3				
1-Octyne	1036.5	1034.1		1030.7				
2-Octyne	1063.0	1063.8		1064.9				
3-Octyne	1013.1	1012.5		1011.7				
4-Octyne	1000.2	999.0		997.6				
1-Nonyne		1134.8	1133.7	1132.9	1132.0			
2-Nonyne		1161.5	1163.0	1163.0	1163.4			
3-Nonyne		1109.4	1109.5	1108.8	1108.1			
4-Nonyne		1095.0	1095.8	1195.2	1094.5			
1-Decyne		1235.3	1234.0	1233.4	1232.8	1231.5		
2-Decyne		1261.7	1262.7	1263.4	1263.7	1265.2		
3-Decyne		1207.7	1207.4	1207.4	1207.3	1207.0		
4-Decyne		1192.0	1192.2	1192.1	1192.0	1192.2		
5-Decyne		1190.5	1190.7	1190.8	1190.9	1191.3		
1-Undecyne			1333.7	1333.4	1333.2	1332.5	1332.0	1331.1
2-Undecyne			1362.1	1362.8	1363.6	1365.0	1365.3	1365.6
3-Undecyne			1305.9	1306.0	1306.2	1306.2	1305.4	1304.8
4-Undecyne			1288.6	1288.9	1289.2	1289.6	1288.8	1289.3
5-Undecyne			1285.5	1285.7	1286.0	1286.8	1286.5	1286.4
1-Dodecyne			1434.0	1433.9	1433.8	1433.1	1432.5	1432.6
2-Dodecyne			1463.0	1463.6	1464.2	1465.3	1465.5	1466.6
3-Dodecyne			1405.7	1405.6	1405.5	1405.5	1405.3	1405.0
4-Dodecyne			1387.0	1387.2	1387.1	1387.7	1388.0	1388.5
5-Dodecyne			1382.8	1383.0	1383.2	1383.8	1384.2	1384.3
6-Dodecyne			1381.3	1381.6	1381.8	1382.5	1382.7	1383.0
1-Tridecyne				1533.1	1533.0	1532.9	1532.3	1533.2
2-Tridecyne				1562.5	1563.3	1565.1	1565.2	1566.7
3-Tridecyne				1504.7	1504.8	1505.0	1504.9	1505.3
4-Tridecyne				1486.1	1486.4	1486.8	1486.7	1486.8
5-Tridecyne				1479.8	1480.3	1481.2	1481.3	1482.5
6-Tridecyne				1476.9	1477.5	1478.6	1478.8	1479.7
1-Tetradecyne				1632.7	1632.9	1633.1	1632.2	1633.2
2-Tetradecyne				1663.8	1664.3	1665.7	1665.4	1666.9
3-Tetradecyne				1604.2	1604.3	1604.9	1604.2	1604.9
4-Tetradecyne				1584.5	1584.9	1585.8	1585.5	1586.5
5-Tetradecyne				1577.7	1578.5	1579.7	1579.5	1580.7
6-Tetradecyne				1573.6	1574.3	1575.6	1575.6	1576.8
7-Tetradecyne				1571.5	1572.3	1574.0	1574.0	1575.3

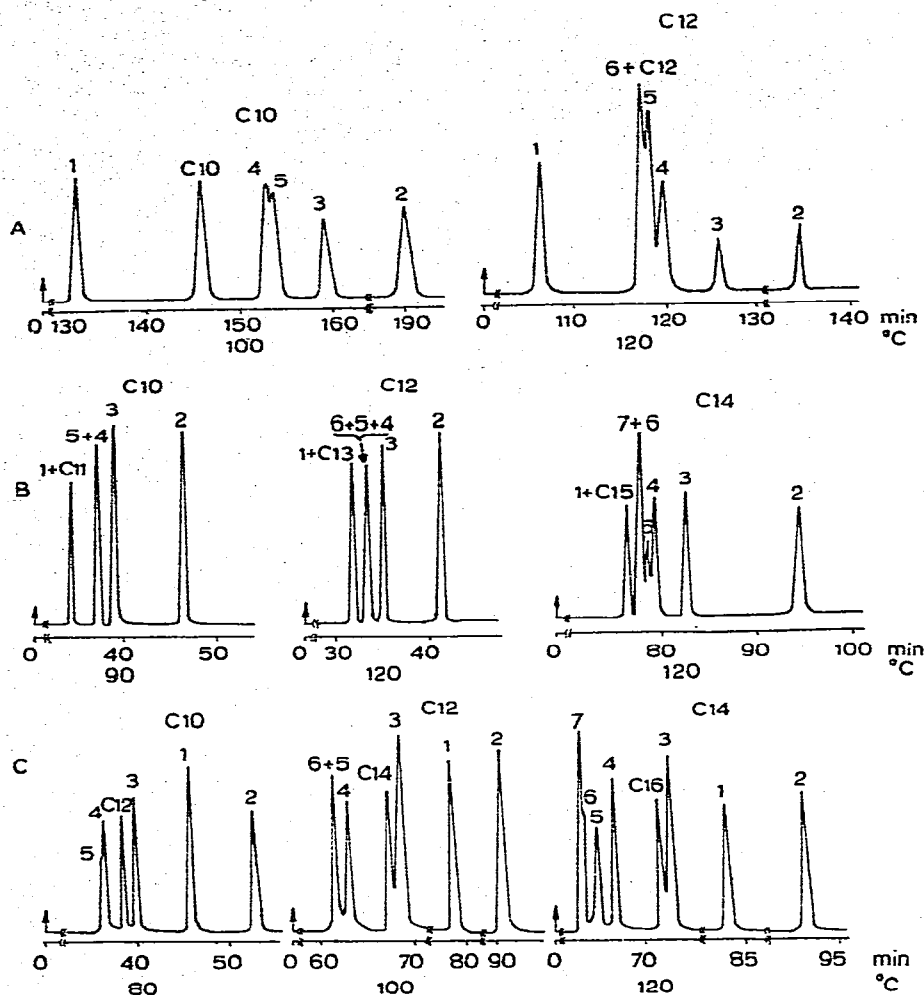


Fig. 1. Chromatograms of the positional isomers of C_{10} , C_{12} and C_{14} *n*-alkynes in the presence of the corresponding *n*-alkanes. Stationary phase: A, squalane; B, polyphenyl ether; and C, polyethylene glycol 4000. On PEG the carrier gas was hydrogen. The peaks are numbered according to the position of the triple bond in the molecule.

of the possibility of formation of cyclic arrangements due to intramolecular interactions⁸. The same effects may be present in alkynes. From Table VIII, it can be seen that the I_{CH_2} values decreased as the triple bond shifted to the centres of the molecules; for 1- and 2-alkynes of C_7 - C_{14} the I_{CH_2} values are 98-102 i.u., and for 5- and 6-alkynes of C_{12} - C_{14} the corresponding values are 95-98 i.u.

The values of the retention index reported are useful for the identification of *n*-alkynes by GC and GC-mass spectrometry, and their dependences on *n* permit the values of higher homologues to be calculated. The trends in *I* with temperature and the correlations between the retention index increments and molecular structure will be discussed in a subsequent paper⁹. Our later experiments have shown that when

TABLE VI

DIFFERENCES BETWEEN I VALUES OF CHARACTERISTIC PAIRS OF n -ALKYNES AT 110°

Number of carbon atoms in the molecule	Phase	Position of triple bond					
		1, 2	2, 3	3, 4	4, 5	5, 6	6, 7
Squalane							
6		54.5	18.5				
7		57.8	26.2				
8		57.7	25.1	6.0			
9		56.5	25.9	5.0			
10		56.6	27.5	6.5	-1.2		
11		55.9	27.7	7.6	0.5		
12		55.4	28.4	8.1	1.6	1.4	
Apiezon L							
10		57.2	32.1	7.5	-1.1		
11		56.8	32.6	8.3	0.8		
12*		55.3	34.1	7.8	1.2	1.4	
13*		55.1	34.8	8.7	1.6	2.9	
14*		55.0	35.8	8.0	3.0	2.8	0.9
Polyphenyl ether							
9		64.2	35.1	10.5			
10		65.5	37.1	10.9	0.1		
11		64.5	37.0	11.6	0.7		
12		64.6	38.1	12.8	0.8	0.1	
13		65.0	38.4	13.9	1.3	1.8	
14		66.3	39.2	13.9	2.5	2.9	1.7
Polyethylene glycol 4000							
6		33.2	35.1				
7		35.8	54.5				
8		34.2	53.2	14.1			
9		30.1	54.2	13.6			
10		30.0	56.0	15.3	1.3		
11		29.4	56.8	17.1	3.2		
12		29.7	58.0	18.4	4.2	1.4	
13		29.4	57.8	18.6	6.3	2.9	
14		31.1	59.6	19.7	6.8	4.1	2.1

* At 150°.

TABLE VII

CONSTANTS a AND b OF THE EQUATION $I = a + bn$ AT 110°

Compounds	SQ		ApL*		PPE		PEG	
	a	b	a	b	a	b	a	b
1-Alkynes	-16.54	100.07	-4.90	100.03	105.52	99.78	232.35	100.09
2-Alkynes	40.51	99.99	50.66	100.00	169.51	99.85	263.94	99.92
3-Alkynes	26.18	98.74	23.60	99.39	140.73	99.09	217.50	99.00
4-Alkynes	26.28	98.06	21.38	98.94	138.36	98.22	215.31	97.69
5-Alkynes	39.32	96.85	33.38	97.87	143.93	97.68	228.44	96.19
6-Alkynes			35.08	97.55				

* At 150°.

TABLE VIII

CONTRIBUTIONS OF ONE METHYLENE GROUP TO THE RETENTION INDICES (I_{CH_2}) OF C_2 - C_{14} *n*-ALKYNES AT 110° I values for C_5 - C_9 *n*-alkynes at 86° were taken from ref. 1.

Number of carbon atoms in the molecule	Phase	Triple bond position					
		1	2	3	4	5	6
Squalane							
3 → 4		86.6					
4 → 5		99.0	84.8				
5 → 6		102.4	95.2				
6 → 7		100.3	103.6	95.9			
7 → 8		99.5	99.4	100.5			
8 → 9		100.4	99.2	98.4	99.4		
9 → 10		100.1	100.2	98.6	97.1		
10 → 11		100.0	99.3	99.1	98.0	96.3	
11 → 12		100.2	99.7	99.0	98.5	97.4	
Apiezon L							
10 → 11		99.9	99.5	99.0	98.2	96.3	
11 → 12*		100.0	99.7	99.5	98.7	98.2	
12 → 13*		100.3	100.1	99.4	98.5	98.1	96.6
13 → 14*		100.2	100.1	99.1	99.8	98.4	98.5
Polyphenyl ether							
9 → 10		100.1	101.4	99.4	99.0		
10 → 11		99.6	98.6	98.7	98.0	97.4	
11 → 12		99.8	99.9	98.8	97.6	97.5	
12 → 13		99.7	100.1	99.8	98.7	98.2	96.5
13 → 14		99.4	100.7	99.9	99.9	98.7	97.6
Polyethylene glycol 4000							
6 → 7		101.9	104.5	85.1			
7 → 8		101.7	100.1	101.4			
8 → 9		102.2	98.1	97.1	97.6		
9 → 10		100.5	100.4	98.6	96.9		
10 → 11		100.0	99.4	98.6	96.8	94.9	
11 → 12		100.5	100.8	99.6	98.3	97.3	
12 → 13		99.2	98.9	99.1	98.9	96.8	95.3
13 → 14		99.6	101.3	99.5	98.4	97.9	96.7

* At 150°.

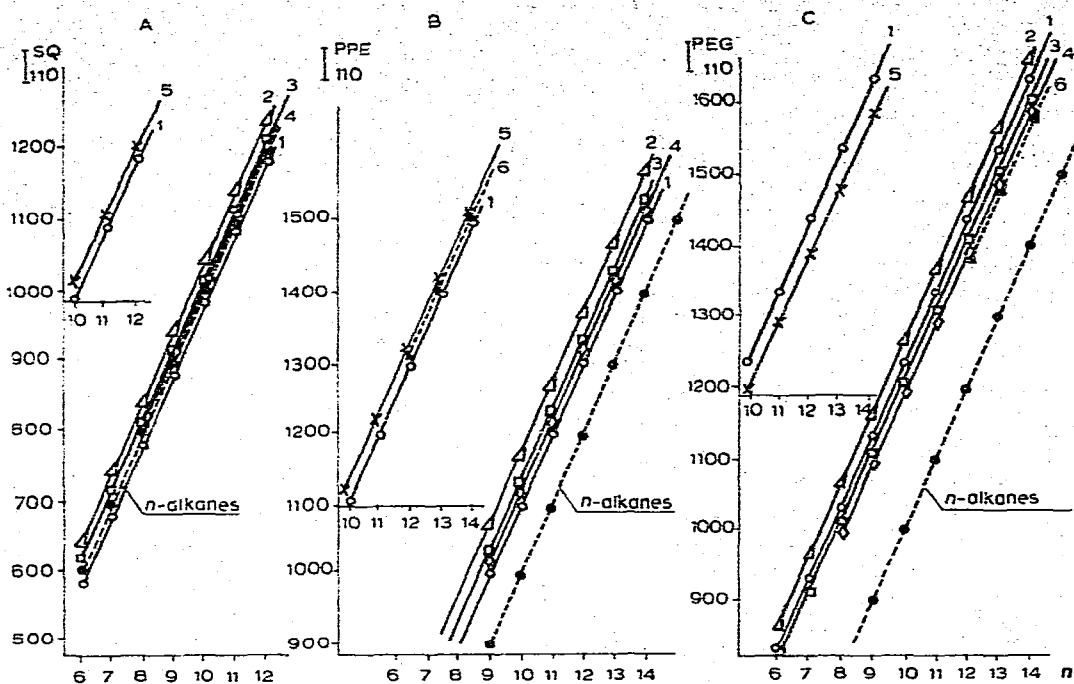


Fig. 2. Dependences of I on the number of carbon atoms, n , in the molecule at 110° . Stationary phases as in Fig. 1. The lines are numbered according to the position of the triple bond in the molecule e.

hydrogen is used as the carrier gas the absolute retention times of n -alkynes, as with n -alkenes⁸, are shorter compared with those obtained when the carrier gas is helium or nitrogen. Lower column temperatures may therefore be used with hydrogen, leading to better separation of isomers. The use of hydrogen as carrier gas is recommended for the analysis of n -alkynes with high boiling points.

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