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CAPILLARY GAS CHROMATOGRAPHY OF *n*-ALKYNES

III. CORRELATION OF RETENTION INDEX INCREMENTS WITH MOLECULAR STRUCTURE

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SUMMARY

n-Alkynes have characteristic retention index (I) increments (H and ΔI, where $H = I_{n\text{-alkyne}} - I_{n\text{-alkane}}$ and $\Delta I = I^{polar} - I^{non\text{-}polar}$) that permit the identification of positional isomers. ΔI increments are useful for the differentiation of 1-, 2- and 3-isomers, while for *n*-alkynes with more central positions of the triple bond they are identical. The structural increments for *n*-alkynes depend on the polarity of the liquid phase, the number of carbon atoms and the position of the triple bond in the molecule and temperature. The H and ΔI values for internal *n*-alkynes are markedly higher than those for *n*-alkenes. On squalane the H increments of 1-alkynes and 1-alkenes are nearly identical.

INTRODUCTION

Retention index increments are structural characteristics of a compound that are very useful for identification purposes and the prediction of retention behaviour[1–5]. Up to now, structural increments, H ($I_{n\text{-alkyne}} - I_{n\text{-alkane}}$) and ΔI ($I^{polar} - I^{non\text{-}polar}$), for *n*-alkynes have not been investigated, and studies using squalane (SQ), Apiezon L (ApL), polyphenyl ether (PFE) and polyethylene glycol 4000 (PEG) as stationary phases are reported in this paper.

RESULTS AND DISCUSSION

The structural increments H and ΔI for C_6–C_{14} *n*-alkynes calculated from the data reported earlier[6] are summarized in Tables I and II. It can be seen that the values depend on the polarity of the stationary phase, column temperature, number of carbon atoms and position of the triple bond in a molecule.

H structural increments

The H values increase with increasing polarity of the liquid phase: for the C_6–C_{14} *n*-alkynes the H_{110}^{SQ} values vary from −16 to +42 index units (i.u.), H_{110}^{PFE} from 102 to 169 i.u. and H_{110}^{PEG} from 172 to 265 i.u.

TABLE I

H STRUCTURAL INCREMENTS OF C_6–C_{14} *n*-ALKYNES

Compound	*Squalane (110°)*	*Apiezon L (150°)*	*Polyphenyl ether*		*Polyethylene glycol 4000*	
			110°	*150°*	*110°*	*150°*
1-Hexyne	−16.1				227.1	
1-Heptyne	−15.8				229.0	
1-Octyne	−16.3				230.7	
1-Nonyne	−15.9		103.4		232.9	
1-Decyne	−15.8		103.5		233.4	
1-Undecyne	−15.8		103.1	105.3	233.4	232.0
1-Dodecyne	−15.6	−4.8	102.9	104.7	233.9	232.5
1-Tridecyne		−4.5	102.6	104.7	233.1	232.3
1-Tetradecyne		−4.3	102.0	104.8	232.7	232.2
2-Hexyne	38.4				260.3	
2-Heptyne	42.0				264.8	
2-Octyne	41.4				264.9	
2-Nonyne	40.6		167.6		263.0	
2-Decyne	40.8		169.0		263.4	
2-Undecyne	40.1		167.6	169.6	262.8	265.3
2-Dodecyne	39.8	50.5	167.5	170.5	263.6	265.5
2-Tridecyne		50.6	167.6	170.3	262.5	265.2
2-Tetradecyne		50.7	168.3	170.3	263.8	265.4
3-Hexyne	19.9				225.2	
3-Heptyne	15.8				210.3	
3-Octyne	16.3				211.7	
3-Nonyne	14.7		132.5		208.8	
3-Decyne	13.3		131.9		207.4	
3-Undecyne	12.4		130.6	131.3	206.0	205.4
3-Dodecyne	11.4	16.4	129.4	130.1	205.6	205.3
3-Tridecyne		15.8	129.2	129.4	204.7	204.9
3-Tetradecyne		14.9	129.1	129.1	204.2	204.2
4-Octyne	10.3				197.6	
4-Nonyne	9.7		122.0		195.2	
4-Decyne	6.8		121.0		192.1	
4-Undecyne	4.8		119.0	121.2	188.9	188.8
4-Dodecyne	3.3	8.6	116.6	119.0	187.2	188.0
4-Tridecyne		7.1	115.3	117.2	186.1	186.7
4-Tetradecyne		6.9	115.2	116.5	184.5	185.5
5-Decyne	8.0		120.9		190.8	
5-Undecyne	4.3		118.3	119.7	185.7	186.5
5-Dodecyne	1.7	7.4	115.8	117.6	183.0	184.2
5-Tridecyne		5.5	114.0	115.5	179.8	181.3
5-Tetradecyne		3.9	112.7	114.8	177.7	179.5
6-Dodecyne	0.3	6.0	115.7	117.0	181.6	182.7
6-Tridecyne		2.6	112.2	115.2	176.9	178.8
6-Tetradecyne		1.1	109.8	112.3	173.6	175.6
7-Tetradecyne		0.2	108.1	111.2	171.5	174.0

TABLE II

ΔI STRUCTURAL INCREMENTS OF C_6–C_{12} *n*-ALKYNES

Compound	*Position of triple bond*											
	1	*2*	*3*	*4*	*5*	*6*	*1*	*2*	*3*	*4*	*5*	*6*
	$\Delta I = I_{110}^{PFE-SQ}$						$\Delta I = I_{110}^{PEG-SQ}$					
Hexyne							243.2	221.9	205.3			
Heptyne							244.8	222.8	194.5			
Octyne							247.0	223.5	195.4	187.3		
Nonyne	119.3	127.0	117.8	112.3			248.8	222.4	194.1	185.5		
Decyne	119.3	128.2	118.6	114.2	112.9		249.2	222.6	194.1	185.3	182.8	
Undecyne	118.9	127.5	118.2	114.2	114.0		249.2	222.7	193.6	184.1	181.4	
Dodecyne	118.5	127.7	118.0	113.3	114.1	115.4	249.5	223.8	194.2	183.9	181.3	181.3

In general, the *H* values decrease in homologous series (Fig. 1) owing to the decrease in the relative contribution of the triple bond to the intermolecular interaction with lengthening of the alkyl chain in the molecule. Lower *H* values are observed for 2-hexyne and 3-heptyne on SQ and PEG. This phenomenon is similar to the anomalously low *H* values of 1-pentene, *cis*- and *trans*-2-hexenes and *trans*-3-heptene on SQ, which were explained in terms of their capability to form cyclic arrangements by intramolecular orbital interactions[5]. The negative *H* values of 1-alkynes on squalane are nearly independent of the chain length, varying from −16.1 to −15.6 for the C_6–C_{12} series at 110°. In the group of 1-alkynes on PEG, the C_6–C_8 compounds have lower *H* values (227–231 i.u.) than the higher homologues (233 i.u.).

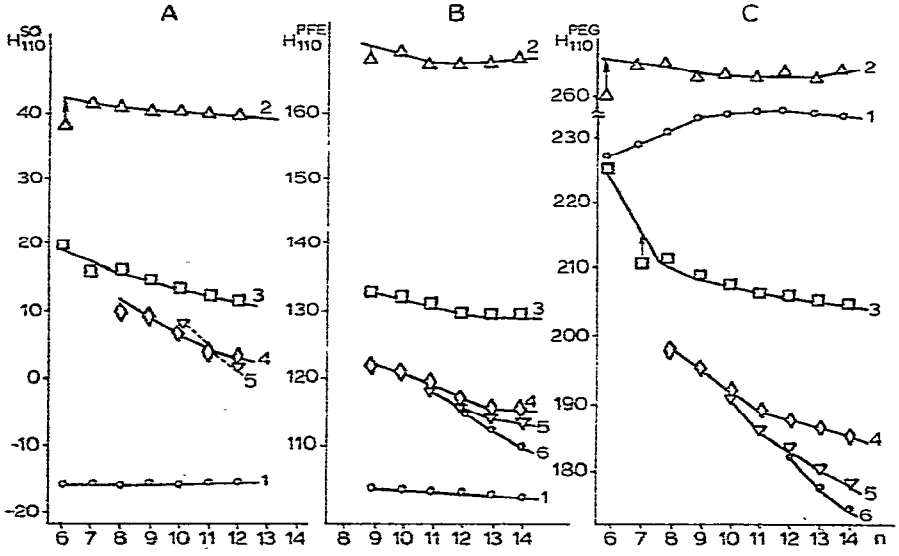

Fig. 1. Dependence of *H* structural increments on the number of carbon atoms in a molecule (*n*) for homologous series of *n*-alkynes at 110°. A, squalane; B, polyphenyl ether; C, polyethylene glycol 4000. The numbers on the lines indicate the positions of the triple bonds.

The H increments for internal n-alkynes with identical chain lengths decrease as the triple bond shifts towards the centre of the molecule, being greatest for 2-alkynes (except that on squalane 5-decyne has a higher increment value than 4-decyne).

ΔI structural increments

As can be seen from Table II, at a given temperature the ΔI values depend appreciably on the position of the triple bond in the molecule and the polarity of the liquid phase. The number of carbon atoms in the molecule has only a slight effect on the ΔI values.

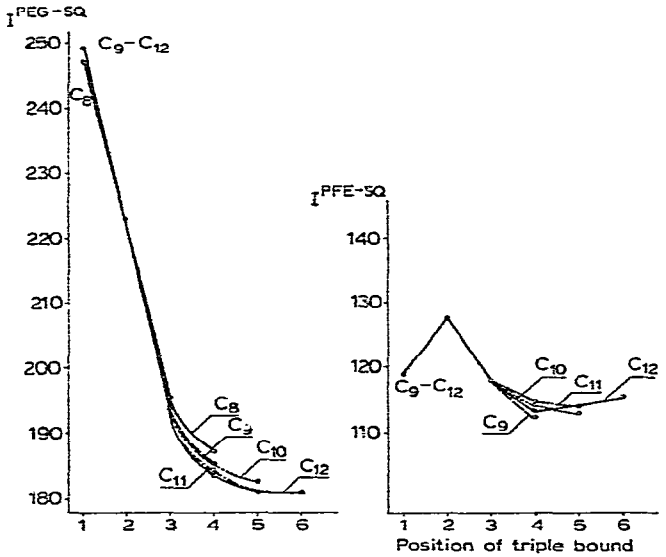

Fig. 2. Dependence of ΔI structural increments of C_8–C_{12} n-alkynes on the position of the triple bond in the molecule at 110°.

The I_{110}^{PEG-SQ} values decrease in agreement with the shift of the triple bond towards the centre of molecule (up to the fifth carbon atom) owing to the increase in the shielding effect with lengthening of the n-alkyl chain from C_1 to C_4 on the dipole–dipole interaction between n-alkynes and the polar liquid phase. The highest I_{110}^{PEG-SQ} values among positional isomers with identical chain lengths are found for 1-alkynes (Fig. 2) .This result can be explained in terms of the formation of hydrogen bonds between 1-alkynes and PEG molecules, owing to the presence of the acidic hydrogen atom at the highly electronegative first carbon atom in 1-alkynes and the proton-accepting oxygen atoms in the liquid phase. The largest decrease in the I_{110}^{PEG-SQ} values is observed with the shift of the triple bond from the first to the second and third carbon atoms. With further shift of triple bond towards the centre of a molecule the changes in I_{110}^{PEG-SQ} values are smaller, and remain nearly constant for compounds with the triple bond in the 5-position and nearer to the centre of the molecule. The I_{110}^{PEG-SQ} values are about twice those of I_{110}^{PFE-SQ} (Table 2).

In a similar manner to I^{PEG-SQ}, the I^{PFE-SQ} values for internal n-alkynes with

TABLE III

CHARACTERISTIC STRUCTURAL INCREMENTS OF RETENTION INDICES OF C_9–C_{12} *n*-ALKYNES AT 110°

Compound	H_{110}^{SQ}	H_{110}^{PFE}	H_{110}^{PEG}	I_{110}^{PEG-SQ}	I_{110}^{PFE-SQ}
1-Alkynes	−15.6–−15.9	102.9–103.5	232.9–233.9	248.8–249.5	118.5–119.3
2-Alkynes	39.8– 40.8	167.5–169.0	262.8–263.6	222.4–223.8	127.0–128.2
3-Alkynes	11.4– 14.7	129.4–132.5	205.6–208.8	193.6–194.2	117.8–118.6
4-Alkynes	3.3– 9.7	116.6–122.0	187.2–195.2	183.9–185.5	112.3–114.2
5-Alkynes	1.7– 8.0	115.8–120.9	183.0–190.8	181.3–182.8	112.9–114.1
6-Dodecyne	0.3	115.7	181.6	181.3	115.4

TABLE IV

CHARACTERISTIC STRUCTURAL INCREMENTS OF RETENTION INDICES OF C_{12}–C_{14} *n*-ALKYNES AT 150°

Compound	H_{150}^{ApL}	H_{150}^{PFE}	H_{150}^{PEG}	$I_{150}^{PEG-ApL}$	$I_{150}^{PFE-ApL}$
1-Alkynes	−4.3–−4.8	104.7–104.8	232.2–232.5	236.5–237.3	109.1–109.5
2-Alkynes	50.5– 50.7	170.3–170.5	265.2–265.5	214.6–215.0	119.6–120.0
3-Alkynes	14.9– 16.4	129.1–130.1	204.2–205.3	188.9–189.3	113.6–114.2
4-Alkynes	6.9– 8.6	116.5–119.0	185.5–188.0	178.6–179.6	109.6–110.4
5-Alkynes	3.9– 7.4	114.0–117.6	179.5–184.2	175.6–176.8	110.0–110.2
6-Alkynes	1.1– 6.0	112.3–117.0	175.6–182.7	174.5–176.7	111.0–112.6
7-Tetradecyne	0.2	111.2	174.0	173.8	111.0

identical chain lengths decrease with the shift of the triple bond towards the centre of a molecule (except for *n*-dodecynes the increase in I^{PFE-SQ} with the shift of the triple bond from position 4 to 6 is found). The highest I_{110}^{PFE-SQ} values are observed for 2-alkynes, whereas 1- and 3-alkynes have close (lower) values of I^{PFE-SQ}.

In Tables III and IV the characteristic H and ΔI values for C_9–C_{12} *n*-alkynes at 110° and C_{12}–C_{14} *n*-alkynes at 150°, respectively, are given.

From these results it is evident that the H and ΔI increments for *n*-alkynes are characteristic of these compounds. They differ markedly from those of *n*-alkenes[1,5,7] (except that the H values of 1-alkynes and 1-alkenes are nearly identical on squalane) and provide useful additional structural information about unknown compounds. Further, they can be used in the calculation of the contribution of triple bonds to I when predicting retention indices on the basis of molecular structure.

The temperature dependences of I reported in ref. 8 enable one to calculate the structural increments at different temperatures.

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