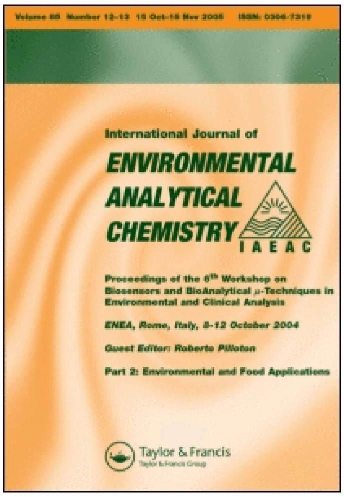

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Analysis of Complex Mixtures of Aromatic Hydrocarbons. Relations between Retention Index and Molecular Structure†

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Relationships between Kováts indices on nonpolar stationary phases and the structure of alkyl- and alkenylbenzenes, defined by the molecular connectivity or connectivity index, have been established.

Almost all components of aromatic naphthas are included in the different linear equations which relate both empirical indices. The constant terms of the straight lines depend on the nature and position of the substituents in the benzene ring. Substituents in *para* position do not influence each other, allowing the study of the effect of its nature on the ratio $\delta I/\Delta\chi$.

Equations for different series of compounds, including *n*-alkyl- and 1,4-di-*n*-alkylbenzene homologous series, are calculated in order to support its identification in aromatic naphthas.

KEY WORDS: Gas chromatography, Kováts indices, molecular connectivity, molecular structure, aromatic hydrocarbons.

INTRODUCTION

Molecular connectivity is a concept intended for the quantification of the topology of molecules. It was introduced by Randić[1] and widely described by Kier and co-workers[2–4] through the topological branching index, which shows correlations with several molecular properties. This topological branching index, also called connectivity index, "χ", has been used by Kaliszan and co-workers[5–8] to investigate the relationships with

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the chromatographic behaviour of several types of organic compounds, finding good correlations with chromatographic parameters such as the Kováts index, "I", particularly when nonpolar stationary phases are used.

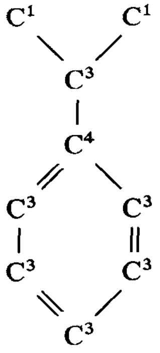
It is known that "I" values are related with the interactions between the solute molecules and the stationary phase. When saturated hydrocarbons are chromatographed on nonpolar stationary phases, only dispersion forces are significant. In this case, the molecular connectivity is able to describe the chromatographic behaviour more exactly than any other empirical parameter.[9] In addition connectivity indices are very easy to calculate.

Aromatic naphthas are complex industrial products whose principal components are alkylbenzenes. Since we deal with aromatic hydrocarbons which are compounds with low polarity, it is supposed that if they are chromatographed on nonpolar stationary phases, in order to minimize the polar interactions, it will be possible to obtain a considerable help in the identification of such components from the relationships between chromatographic retention and connectivity.

The present paper deals with our investigation concerning the relationships between Kováts indices and connectivity indices of alkylbenzenes on squalane at 100°C and alkenylbenzenes on methylsilicone (SE-30) at 65°C.

EXPERIMENTAL

The connectivity index was calculated according to the Kier and Hall's[4] equation $\chi=\Sigma(\delta i\cdot\delta j)^{-1/2}$ where δi and δj are the number of nonhydrogen bonds of the bonded "*i*" and "*j*" carbons. For example, connectivity of isopropylbenzene is calculated as follows:



$$\chi=1/(1.3)^{1/2}+1/(1.3)^{1/2}+1/(4.3)^{1/2}+1/(4.3)^{1/2}+1/(4.3)^{1/2}$$

$$+1/(3.3)^{1/2}+1/(3.3)^{1/2}+1/(3.3)^{1/2}+1/(3.3)^{1/2}=3.353$$

"*I*" values on squalane at 100°C are available in the literature[10–13] although, when it was possible, data from Engewald and Wennrich[11] were preferably used in order to secure homogeneity of the results. All data about alkenylbenzenes were taken from Svob and Deur-Siftar[12] who obtained them on methylsilicone (SE-30) at 65°C.

RESULTS

Data about alkylbenzenes on squalane and alkenylbenzenes on methylsilicone (SE-30) are presented in Figure 1. This figure shows that there are different linear relationships between "I" and "χ" in both nonpolar phases.

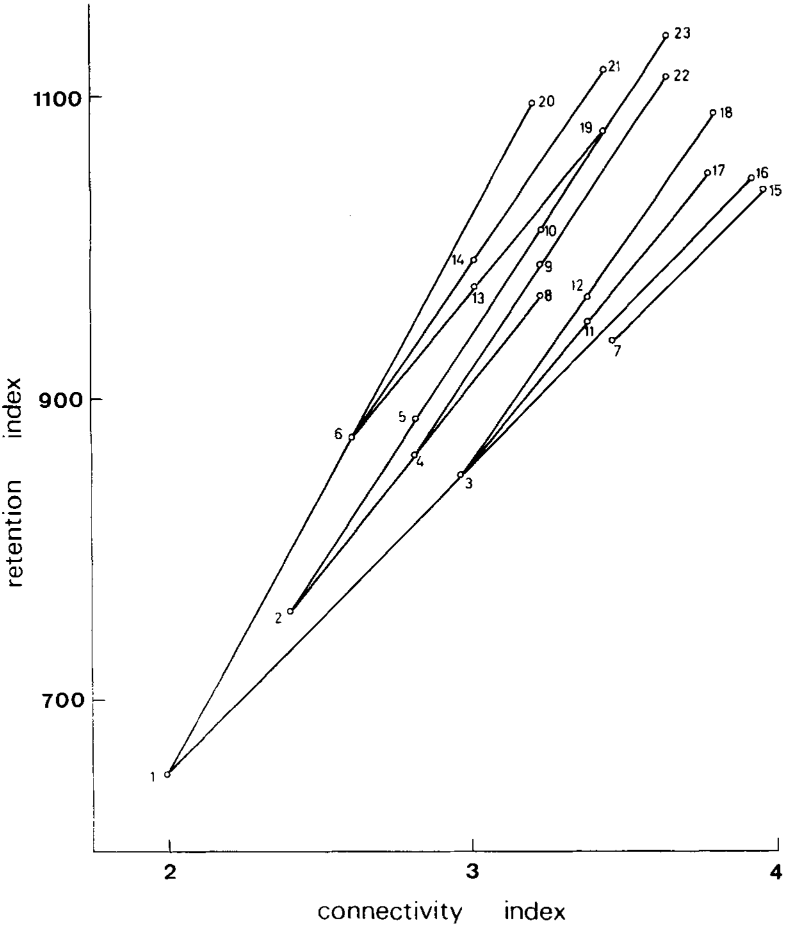


FIGURE 1 Plot of Kováts indices "I" against connectivity indices "χ" for alkylbenzenes on squalane at 100°C and alkenylbenzenes on methylsilicone (SE-30) at 65°C. Numbers correspond to the components quoted in Tables I–IV.

The constant terms of the straight regression lines depend on the nature of the substituents and their relative positions in the benzene ring. The only lines where benzene is included appear defined only by three points belonging to the series: benzene, R-benzene and 1,4-RR-benzene. The linearity of these points in the plot "I" versus "χ", states that the values $\delta I/\Delta\chi$ ($\delta I = I_2 - I_1$ and $\Delta\chi = \chi_2 - \chi_1$) do not vary when a second substituent is introduced in the *para position. On the contrary when a second substituent enters in an ortho* position the ratio $\delta I/\Delta\chi$ increases, whereas a very small decrease is observed if the substituent occurs in a *meta* position.

For studying the dependency between $\delta I/\Delta\chi$ values and the nature of the substituent, the series of 1,4-disubstitutions, in which the substituents are not influenced each other, are appropriated. The corresponding equations and their respective constants are shown in Table I. For alkylbenzenes the $\delta I/\Delta\chi$ values increase in the following order:

R = methyl > ethyl > *n*- > tert- > iso- > sec-alkyl

As it is well known,[11] the value of I_{CH_2} (index difference per methylen group) from the homologous series of *n*-alkylbenzenes present a minimum for the second and the third addition of a methylene group (Figure 2). On

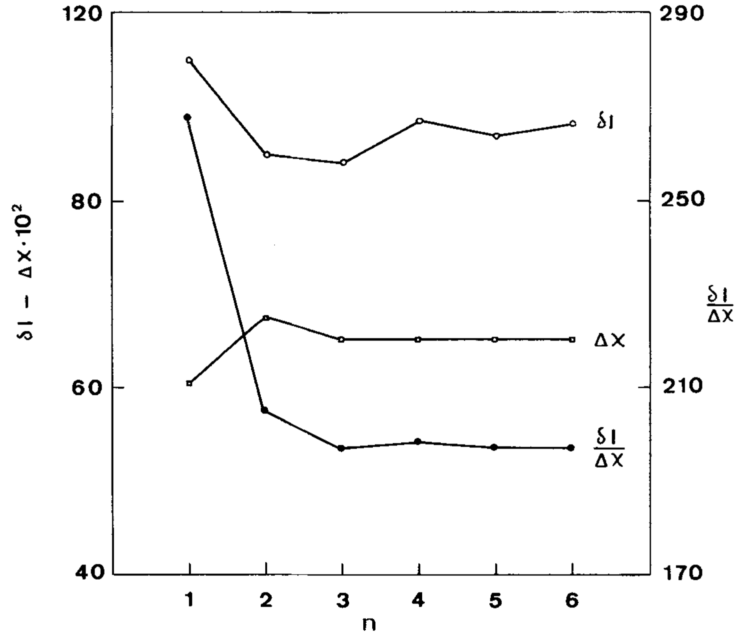


FIGURE 2 Dependence of index increments per CH_2-group (on squalance at 100°C) (δI), connectivity increments ($\Delta\chi$) and $\delta I/\Delta\chi$, on carbon number (n) of alkyl benzene substituent.

TABLE I

Equations $I = f(\chi)$ for series benzene, R-benzene and 1,4-RR-benzene

Components (see Figure 1)	I	χ	$I = a\chi + b$
benzene (1)	654.8	2.000	$a = 362.4$
vinylbenzene (6)	874.9	2.606	$b = -69.9$
1,4-divinylbenzene (20)	1095.9	3.217	$r = 1.00000$
benzene (1)	650.5	2.000	$a = 260.4$
methylbenzene (2)	760.1	2.409	$b = 131.6$
1,4-dimethylbenzene (4)	864.6	2.822	$r = 0.99986$
benzene (1)	650.5	2.000	$a = 200.7$
ethylbenzene (3)	850.0	2.970	$b = 250.7$
1,4-diethylbenzene (16)	1040.5	3.943	$r = 0.99990$
benzene (1)	650.5	2.000	$a = 191.0$
n-propylbenzene (7)	938.0	3.470	$b = 270.8$
1,4-di-*n*-propylbenzene	1212.5	4.943	$r = 0.99990$
benzene	650.5	2.000	$a = 185.9$
isopropylbenzene	908.4	3.353	$b = 280.8$
1,4-diisopropylbenzene	1154.1	4.709	$r = 0.99989$
benzene (1)	650.5	2.000	$a = 192.8$
n-butylbenzene (15)	1036.8	3.970	$b = 267.0$
1,4-di-*n*-butylbenzene	1410.8	5.943	$r = 0.99995$
benzene	650.5	2.000	$a = 189.8$
tert-butylbenzene	971.7	3.659	$b = 272.9$
1,4-di-tert-butylbenzene	1281.3	5.323	$r = 0.99993$
benzene	650.5	2.000	$a = 172.7$
sec-butylbenzene	990.2	3.892	$b = 309.3$
1,4-di-sec-butylbenzene	1304.3	5.785	$r = 0.99974$
benzene	650.5	2.000	$a = 179.8$
isobutylbenzene	991.3	3.825	$b = 295.1$
1,4-diisobutylbenzene	1307.7	5,655	$r = 0.99975$

the other hand, the introduction of a methyl group in the benzene ring increases the "χ" value by 0.409, the first methylene group by 0.561 and the second and following by 0.500. Consequently, the $\delta I/\Delta\chi$ value decreases when the second methylene group enters, becoming constant after the propylbenzene.

The order within each group of the alkylbenzene isomers is explained because of the different variation of their retention indices (n- > iso- > sec- > tert-) and their connectivities (n- > sec- > iso > tert-).

Effects of the substituents in ortho position

When a second group enters in an *ortho* position it originates an increase in the $\delta I/\Delta\chi$ ratio respective of the value determined by the first substituent, whatever the nature of both groups is.

In Table II it is shown that the compound series methyl-, 1,2-dimethyl-, 1,2,3-trimethyl-, 1,2,3,4-tetramethyl- and pentamethylbenzene defines a straight line, in a plot $I \overset{\text{vs}}{—} \chi$, with a regression coefficient >0.9999, in spite of that the third methyl group enters in an *ortho* or *meta* substituted position. The line belonging to the 1,4-dimethylbenzene and its trimethyl- and tetramethyl- derivatives obtained by consecutive introduction of a methyl group in a carbon atom whose *meta* and *ortho* position are occupied, has the same slope as the preceding line. Both series show again that the substituents have very little influence on *meta* and *para* positions (Table II).

When the methyl group enters in a position flanked by other methyl groups (*ortho* and *ortho* substituted position) the slope of the equation $I = f(\chi)$ increases as a logic consequence of the double influence of the two methyl groups in *ortho* positions. This happens whatever the entering group and the substituent groups are, although the effect is greater when the substituent groups are methyl groups than when they are other alkyl or alkenyl groups.

The plot of the series of trisubstituted benzenes, where two of the substituents are methyl and the other is a vinyl or ethyl group, shows two straight lines almost parallels to the ordinate axis because of the small difference in the "χ" values which these isomers have (Figure 3). The "I" values for the dimethyl-ethyl isomers, fall in the expected order according to the slopes of the lines in Table II, which take on the greatest value when a methyl group is introduced in a position which is *ortho* methylated or flanked by methyl groups.

In the group of the dimethyl-vinyl isomers there are some deviations from the expected order. The most important belong to the 1,3-dimethyl-2-vinylbenzene whose location in the last place of the series has to be considered as an anomaly.

TABLE II

Equations $I=f(\chi)$ for series originated when an R-group enters in an ortho substituted position or in an ortho flanked position. Indices from References 10 and 12.

Components (see Figure 1)	I	χ	$I=a\chi+b$
methylbenzene (2)	756.6	2.409	$a=301.7$
1,2-dimethylbenzene (5)	882.9	2.827	$b=30.3$
1,2,3-trimethylbenzene (10)	1011.1	3.243	$r=0.99998$
1,2,3,4-tetramethylbenzene (23)	1133.9	3.660	
pentamethylbenzene	1260.1	4.077	$r=0.99938$
1,4-dimethylbenzene (4)	860.8	2.822	$a=301.0$
1,2,4-trimethylbenzene (9)	985.5	3.239	$b=11.2$
1,2,3,5-tetramethylbenzene (22)	1111.8	3.656	$r=1.00000$
ethylbenzene (3)	846.9	2.970	$a=269.0$
1-methyl-2-ethylbenzene (12)	963.9	3.388	$b=49.6$
1,2-dimethyl-3-ethylbenzene (18)	1071.2	3.804	$r=0.99972$
vinylbenzene (6)	874.9	2.606	$a=290.7$
1 methyl-2-vinylbenzene (14)	989.0	3.024	$b=114.9$
1,3-dimethyl-2-vinylbenzene (21)	1117.9	3.442	
1,3,5-trimethylbenzene (8)	969.0	3.234	$a=352.0$
1,2,3,5-tetramethylbenzene (22)	1113.1	3.656	$b=-171.7$
pentamethylbenzene	1260.1	4.077	$r=0.99987$
hexamethylbenzene	1415.0	4.500	
1,3-dimethylbenzene (4)	864.8	2.822	$a=351.8$
1,2,3-trimethylbenzene (10)	1012.9	3.243	
1-methyl-3-ethylbenzene (11)	947.9	3.383	$a=331.4$
1,2-dimethyl-3-ethylbenzene (18)	1087.4	3.804	
1-methyl-3-vinylbenzene (13)	974.0	3.019	$a=291.0$
1,2-dimethyl-3-vinylbenzene	1097.1	3.442	

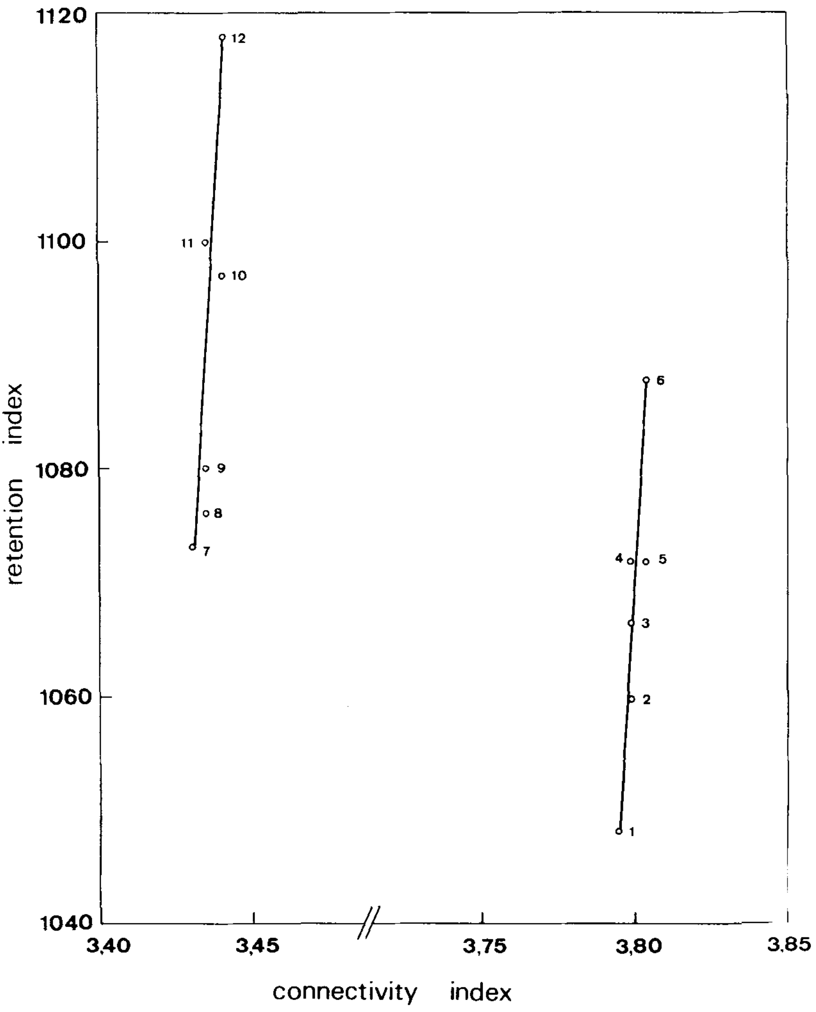


FIGURE 3 Relationships between "*I*" and "χ" in the series of dimethyl-ethylbenzenes and dimethyl-vinylbenzenes.

(1) 1,3-dimethyl-5-ethylbenzene;	(2) 1,4-dimethyl-2-ethylbenzene;
(3) 1,3-dimethyl-4-ethylbenzene;	(4) 1,2-dimethyl-4-ethylbenzene;
(5) 1,3-dimethyl-2-ethylbenzene;	(6) 1,2-dimethyl-3-ethylbenzene;
(7) 1,3-dimethyl-5-vinylbenzene;	(8) 1,4-dimethyl-2-vinylbenzene;
(9) 1,3-dimethyl-4-vinylbenzene;	(10) 1,2-dimethyl-3-vinylbenzene;
(11) 1,2-dimethyl-4-vinylbenzene;	(12) 1,3-dimethyl-2-vinylbenzene.

Homologous series of straight chain mono- and 1,4-dialkylbenzenes

As a consequence of the variation of "I" and "χ" shown in Figure 2, the correlation decreases when toluene and ethylbenzene are included. However, when the series start from the *n*-propylbenzene, the regression coefficient is >0.9999 for all series shown in Table III.

TABLE III

Equations $I=f(\chi)$ for homologous series mono- and 1,4-*n*-dialkylbenzenes

Components (see Figure 1)	I	χ	$I=a\chi+b$
n-propylbenzene (7)	938.0	3.470	$a=195.0$ $b=261.6$ $r=1.00000$
n-butylbenzene (15)	1036.8	3.970	
n-pentylbenzene	1133.0	4.470	
n-hexylbenzene	1231.0	4.970	
1-methyl-4-propylbenzene	1040.2	3.883	$a=195.4$ $b=281.8$ $r=1.00000$
1-methyl-4-butylbenzene	1138.8	4.383	
1-methyl-4-pentylbenzene	1236.3	4.883	
1-methyl-4-hexylbenzene	1333.4	5.383	
1-ethyl-4-propylbenzene	1126.4	4.443	$a=195.8$ $b=257.3$ $r=0.99994$
1-ethyl-4-butylbenzene	1227.1	4.943	
1-ethyl-4-pentylbenzene	1322.1	5.443	
1-ethyl-4-hexylbenzene	1421.1	5.943	
1,4-di-*n*-propylbenzene	1212.5	4.943	$a=198.3$ $b=232.1$ $r=1.00000$
1-propyl-4-butylbenzene	1311.0	5.443	
1-propyl-4-pentylbenzene	1410.8	5.943	

The I_{CH_2} values originated in the sequence toluene-ethylbenzene-*n*-propylbenzene are the same for all 1,4-dialkylbenzene series, for example, for 1-methyl-4-*n*-butyl-, 1-ethyl-4-*n*-butyl- and 1-*n*-propyl-4-*n*-butylbenzene.

Table IV shows other series of alkyl- and alkenylbenzenes with *meta* substitutions, which give also straight lines with very good regression coefficients, therefore they can give support in the identification of components of aromatic naphthas.

TABLE IV

Equations $I = f(\chi)$ for series of *meta* substitutions. Indices from Reference 12

Components (see Figure 1)	I	χ	$I = a\chi + b$
methylbenzene (2)	758.0	2.409	$a = 254.1$
1, 3-dimethylbenzene (4)	863.2	2.822	$b = 146.0$
1, 3, 5-trimethylbenzene (8)	967.6	3.234	$r = 1.00000$
ethylbenzene (3)	847.7	2.970	$a = 243.3$
1-methyl-3-ethylbenzene (11)	948.6	3.383	$b = 125.1$
1, 3-dimethyl-5-ethylbenzene (17)	1048.2	3.794	$r = 1{,}00000$
propylbenzene	936.1	3.470	$a = 235.6$
1-methyl-3-propylbenzene	1033.4	3.883	
isopropylbenzene	908.0	3.353	$a = 228.6$
1-methyl-3-isopropylbenzene	1002.4	3.766	
tert-butylbenzene	972.9	3.659	$a = 214.9$
1-methyl-3-tert-butylbenzene	1055.8	4.072	$b = 184.6$
1, 3-dimethyl-5-tert-butylbenzene	1150.2	4.484	$r = 0.99927$
vinylbenzene (6)	874.0	2.606	$a = 240.0$
1-methyl-3-vinylbenzene (13)	974.0	3.019	$b = 249.4$
1, 3-dimethyl-5-vinylbenzene (19)	1072.9	3.431	$r = 1.00000$
allylbenzene	929.3	3.080	$a = 239.0$
1-methyl-3-allybenzene	1028.0	3.493	
isoallylbenzene	1004.2	3.109	$a = 237.5$
1-methyl-3-isoallylbenzene	1102.3	3.522	

CONCLUSIONS

The multiple relationships found between the chromatographic retention indices on nonpolar stationary phases and the molecular structure, defined by the molecular connectivity, for an extensive series of alkyl- and alkenylbenzenes, the very good correlations between both parameters found for all the series, and the easy calculation of the connectivity indices, make possible to set up a method for the identification of these compounds in environmental or industrial samples, namely in aromatic naphthas.

This method is less time-consuming and has advantages in material requirements and precision over other identification methods based on ΔI, δI or homomorphic factors, and their relations with the polarity of the stationary phase.[11,13,14]

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