

## Short Communication

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# Correlation between gas chromatographic retention indices of linear alkylbenzene isomers and molecular connectivity indices

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(First received April 20th, 1993; revised manuscript received July 13th, 1993)

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### ABSTRACT

The gas chromatographic retention indices of linear alkylbenzene isomers (LABs), with C<sub>10</sub>–C<sub>14</sub> linear alkyl chains were correlated using different molecular connectivity indices. The single linear correlations showed that these do not explain the chromatographic retention of the isomeric structures. Corrected molecular connectivity indices, searching to consider the steric effects produced by the phenyl group on the alkyl chain, showed a good correlation with the retention indices of LABs and a correct elution sequence. Multiple linear correlation with connectivity indices that encode complementary information gives good correlation coefficients and the correct elution sequence of most of the compounds.

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### INTRODUCTION

The existence of a quantitative structure–retention index relationship (QSRR) makes possible the prediction of retention indices of compounds through their chemical structures, or permits the prediction of structures from retention indices [1–3]. Structural information based on the use of topological (graph–theoretical) indices characterizes the molecule by a simple number. In spite of the molecule being described by a one-dimensional parameter (topological index), it is surprising how much relevant structural information is retained in a given topological number index. Many topological indices have been proposed [4–6]. One of the

most useful is the molecular connectivity index introduced by Randić [7] and developed extensively by Kier [8] because of its important applications [9,10]. According to Mihalic and Trinajstić [11], one of the weakest points of these kinds of indices is the lack of discrimination of positional isomers.

The aim of this study was to evaluate the ability of molecular connectivity indices to predict the retention indices of linear alkylbenzene isomers (LABs). The importance of LABs with alkyl carbon numbers of 10–14 is that they are found as residues from incomplete sulphonation and are carried with linear alkylbenzenesulphonates (LAS) in detergents. Recent reviews [12,13] on the presence of LABs in river waters and estuarine sediment cores show that LAB pollution starts from the depth corresponding to the time when LAS detergents began being used

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in the catchment area [13]. LABs consist of isomers that differ in the position of the phenyl group on the alkyl side-chain. For detergents and untreated domestic wastes the relative abundances of isomers with a given alkyl chain length are nearly equal. For river and coastal sediments, however, internal isomers (those having the phenyl attachment toward the middle of the alkyl chain, *e.g.*, 6-C10) dominate over external isomers (those having the phenyl attachment near the end of the alkyl chain, *e.g.*, 2-C10; *n-Cm*, where *n* indicates the position of the benzene ring in the alkyl chain and *m* indicates the number of carbon atoms of the alkyl chain). This difference in isomeric composition has been considered to be caused by selective biodegradation of external isomers relative to internal isomers [13]. In this form, the composition of LABs may provide information on the extent of its biodegradation and it can be used as a molecular tracer of domestic wastes in the environment.

## EXPERIMENTAL

The chromatographic retention indices (*I*) of linear alkylbenzene isomers with C<sub>10</sub>-C<sub>14</sub> alkyl chains (LABs) were reported by Takad and Ishiwatari [12] and Peng *et al.* [3].

The molecular connectivity index path ( $X_p$ ) and cluster ( $X_c$ ,  $X_{pc}$ ) of different orders were calculated by the method of Kier [8] utilizing the Molconn-X computer program for molecular topology analysis [14].

The connectivity indices ( $^1X$ ,  $^2X$ , ...,  $^hX$ ) were calculated according to the Kier's [8] equation:

$$^hX = \sum_{s=1}^t (\delta_i \cdot \delta_j \cdots \delta_{n+1}) \quad (1)$$

where *s* refers to a single path or subgraph of length *h*, *t* is the total number of paths *h* in a graph,  $\delta_i$ ,  $\delta_j$ , ...,  $\delta_{n+1}$  represent values attributed to the adjacent atoms *i* and *j* in the hydrogen-suppressed molecular graph and the superscript *h* on *X* denotes the so-called order of connectivity index. The path connectivity index ( $X_p$ ) with one order conveys more information

about the number of atoms in a molecule and with higher order (2-7) encodes also information about branching.

$X^*$  values are obtained, for example, by taking the difference between the *x* intercept values of the straight lines corresponding to the homologous series (2C10-2C14, 3C10-3C14, 4C10-4C14, 5C10-5C14 and 6C11-6C14) and the *x* intercept values of homologous series (1C10-1C14), decreasing these values of the  $^4X_p$  index.

All calculations of single and multiple linear regression analyses were carried out on an IBM AT/486 computer. To test the quality of the regression equation, the correlation coefficient (*r*), the coefficient of determination ( $r^2$ ) and the test of null hypothesis (*F*-test) were utilized as statistical parameters.

## RESULTS AND DISCUSSION

The values of chromatographic retention indices (*I*) of isomers of LABs with C<sub>10</sub>-C<sub>14</sub> linear alkyl chains [3,12] and their connectivity indices  $^1X$ ,  $^2X$ ,  $^3X_p$ ,  $^4X_p$ ,  $^5X_p$ ,  $^6X_p$  and  $^7X_p$  are given in Table I.

The connectivity indices of lower orders,  $^1X$ ,  $^2X$  and  $^3X_p$ , do not distinguish the positional isomers of the aromatic ring; the distinction only occurs from  $^4X_p$ . Considering the unsaturation in the aromatic ring, the valence connectivity indices were applied, but did not improve the distinction of the same isomers.

Although the cluster connectivity indices ( $^3X_c$  and  $^4X_{pc}$ ) encode more information about branching, they do not distinguish the positional isomers 3C, 4C, 5C and 6C of the aromatic ring; the distinction only occurs when the aromatic ring is in the position 1C and 2C of the alkyl chain. It is important to note that the  $I_{SE-54}$  and  $I_{DB-1}$  values decrease when the position of the aromatic ring go from C1 to C<sub>*n*</sub> (*n* = 2, 3, 4, 5 and 6) in the same isomeric series. When the position of the aromatic ring is more internal in the molecule, it interposes between the alkyl chain and the stationary phase and the molecule becomes more symmetrical and more compact, decreasing the interaction surface, and so its chromatographic retention index decreases

TABLE I

MOLECULAR CONNECTIVITY INDICES AND OBSERVED RETENTION INDICES OF LINEAR ALKYL BENZENES WITH C<sub>10</sub>–C<sub>14</sub> LINEAR ALKYL CHAINS ON SE-54 AND DB-1 STATIONARY PHASES

| Compound | $I_{\text{SE-54}}^a$ | $I_{\text{DB-1}}^b$ | $^1X_p$ | $^2X_p$ | $^3X_p$ | $^4X_p$ | $^5X_p$ | $^6X_p$ | $^7X_p$ |
|----------|----------------------|---------------------|---------|---------|---------|---------|---------|---------|---------|
| 1C10     | 100.00               | 1664                | 7.9319  | 5.7676  | 4.1907  | 3.0427  | 2.2077  | 1.1840  | 0.7747  |
| 2C10     | 92.84                | 1588                | 7.8425  | 5.9318  | 4.4676  | 3.1855  | 2.2710  | 1.2025  | 0.7878  |
| 3C10     | 89.37                | 1553                | 7.8805  | 5.7693  | 4.5193  | 3.3888  | 2.4150  | 1.3041  | 0.8549  |
| 4C10     | 87.54                | 1534                | 7.8805  | 5.7962  | 4.4044  | 3.4254  | 2.5587  | 1.3990  | 0.9555  |
| 5C10     | 86.70                | 1526                | 7.8805  | 5.7962  | 4.4233  | 3.3442  | 2.5751  | 1.5413  | 1.0144  |
| 1C11     | 110.00               | 1771                | 8.4319  | 6.1211  | 4.4407  | 3.2195  | 2.3327  | 1.2724  | 0.8372  |
| 2C11     | 102.71               | 1692                | 8.3425  | 6.2854  | 4.7176  | 3.3623  | 2.3963  | 1.2909  | 0.8503  |
| 3C11     | 99.15                | 1656                | 8.3805  | 6.1229  | 4.7693  | 3.5656  | 2.5400  | 1.3925  | 0.9221  |
| 4C11     | 97.15                | 1636                | 8.3805  | 6.1497  | 4.6544  | 3.6022  | 2.6837  | 1.4941  | 0.9893  |
| 5C11     | 96.20                | 1626                | 8.3805  | 6.1497  | 4.6734  | 3.5209  | 2.7096  | 1.5890  | 1.0898  |
| 6C11     | 95.92                | 1620                | 8.3805  | 6.1497  | 4.6734  | 3.5344  | 2.6426  | 1.6480  | 1.1488  |
| 1C12     | 120.00               | 1870                | 8.9319  | 6.4747  | 4.6907  | 3.3963  | 2.4577  | 1.3608  | 0.8997  |
| 2C12     | 112.63               | 1791                | 8.8425  | 6.6389  | 4.9676  | 3.5391  | 2.5213  | 1.3792  | 0.9128  |
| 3C12     | 108.95               | 1755                | 8.8805  | 6.4764  | 5.0193  | 3.7424  | 2.6650  | 1.4809  | 0.9846  |
| 4C12     | 106.09               | 1735                | 8.8805  | 6.5033  | 4.9044  | 3.7790  | 2.8087  | 1.5825  | 1.0565  |
| 5C12     | 105.76               | 1723                | 8.8805  | 6.5033  | 4.9234  | 3.6977  | 2.8346  | 1.6841  | 1.1236  |
| 6C12     | 105.31               | 1719                | 8.8805  | 6.5033  | 4.9234  | 3.7111  | 2.7771  | 1.6957  | 1.2242  |
| 1C13     | 130.00               | 1978                | 9.4319  | 6.8282  | 4.9407  | 3.5730  | 2.5827  | 1.4492  | 0.9622  |
| 2C13     | 122.52               | 1894                | 9.3425  | 6.9925  | 5.2176  | 3.7159  | 2.6463  | 1.4676  | 0.9753  |
| 3C13     | 118.81               | 1854                | 9.3805  | 6.8300  | 5.2693  | 3.9191  | 2.7900  | 1.5693  | 1.0471  |
| 4C13     | 116.59               | 1833                | 9.3805  | 6.8568  | 5.1544  | 3.9557  | 2.9337  | 1.6709  | 1.1190  |
| 5C13     | 115.42               | 1821                | 9.3805  | 6.8568  | 5.1734  | 3.8745  | 2.9596  | 1.7725  | 1.1909  |
| 6C13     | 114.75               | 1814                | 9.3805  | 6.8568  | 5.1734  | 3.8879  | 2.9021  | 1.7908  | 1.2580  |
| 1C14     | 140.00               |                     | 9.9319  | 7.1818  | 5.1907  | 3.7498  | 2.7077  | 1.5376  | 1.0247  |
| 2C14     | 132.46               |                     | 9.8425  | 7.3460  | 5.4676  | 3.8927  | 2.7713  | 1.5560  | 1.0378  |
| 3C14     | 128.67               |                     | 9.8805  | 7.1835  | 5.5193  | 4.0959  | 2.9150  | 1.6577  | 1.1096  |
| 4C14     | 126.37               |                     | 9.8805  | 7.2104  | 5.4044  | 4.1325  | 3.0587  | 1.7593  | 1.1815  |
| 5C14     | 125.01               |                     | 9.8805  | 7.2104  | 5.4234  | 4.0513  | 3.0846  | 1.8609  | 1.2534  |
| 6C14     | 124.20               |                     | 9.8805  | 7.2104  | 5.4234  | 4.0647  | 3.0271  | 1.8792  | 1.3252  |

<sup>a</sup> From ref. 12.<sup>b</sup> From ref. 3.

owing to the steric and conformational effects. It has been indicated that steric and polar rather than hydrophobic interactions take place in GLC separations [15].

The behaviour of the values of the connectivity indices differs. The  $^6X_p$  and  $^7X_p$  indices increase when the phenyl group changes from C1 to C6 because the number of subgraphs for their calculation also increases. A possible interpretation is that not all the subgraphs must be considered to contribute to the retention, taking into account the steric and conformational effects. For this reason,  $^4X_p$ ,  $^5X_p$ ,  $^6X_p$  and  $^7X_p$  do not give good information about these isomers and a

simple linear correlation with  $I$  is not acceptable. Nevertheless, this linear correlation for SE-54 and DB-1 shows a good correlation between the retention indices and connectivity indices for each homologous series (1C10–1C14, . . .). Fig. 1 shows the correlation with  $^7X_p$ . The same results were obtained with  $^1X$ ,  $^2X$ ,  $^3X_p$  with the number of carbon atoms and molecular mass.

However, the difference in the  $x$  intercept values (when  $I = 112$  for SE-54 and  $I = 1740$  for DB-1) may be considered as a measure of the steric or conformational effects on the connectivity indices corresponding to the distinct position of the aromatic ring in the alkyl chains. This

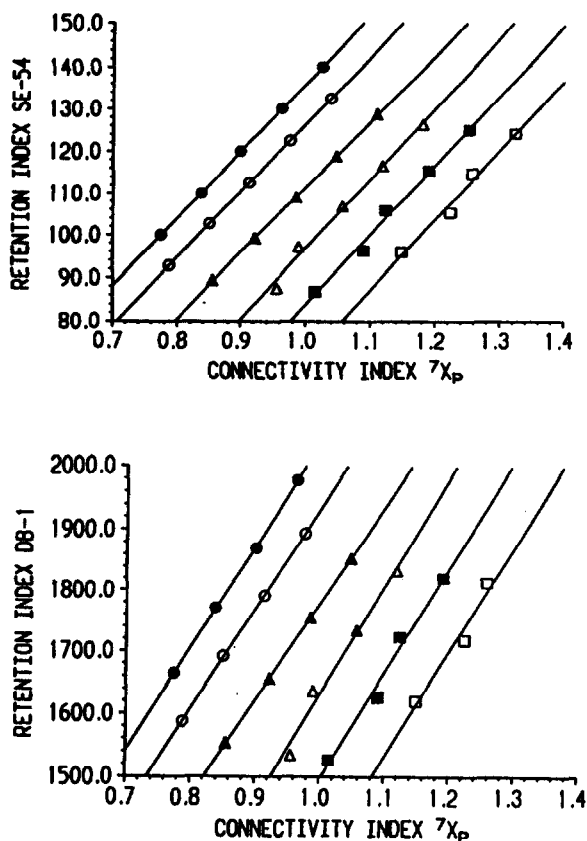


Fig. 1. Correlation between experimental retention indices and molecular connectivity index,  ${}^7X_p$ , for homologous series of linear alkylbenzene isomers: SE-54: ● = 1C10-1C14; ○ = 2C10-2C14; ▲ = 3C10-3C14; △ = 4C10-4C14; ■ = 5C10-5C14; □ = 6C11-6C14. DB-1: ● = 1C10-1C13; ○ = 2C10-2C13; ▲ = 3C10-3C13; △ = 4C10-4C13; ■ = 5C10-5C13; □ = 6C11-6C13.

consideration does not have any sense with respect to the number of carbon atoms, the molecular mass, etc.

With the purpose of correcting for these effects and to obtain an equation that is able to predict the retention and the elution sequence of LABs, a method is proposed. The values of the slopes of the straight lines, for each homologous series, are slightly different. As the steric and conformational effects much be the same, the median slope is utilized, and new  $x$  intercept values can be obtained for each straight line. Taking the difference between the  $x$  intercept values corresponding to the different straight lines and the  $x$  intercept value of 1C10-1C14, on

decreasing these values of the  ${}^7X_p$  index new corrected values,  ${}^7X_p^*$ , are obtained. These new values  ${}^7X_p^*$  correlate in an excellent way with  $I_{SE-54}$  ( $r=0.9975$ ) and with  $I_{DB-1}$  ( $r=0.9954$ ) and give the correct elution sequence for most of the compounds (Fig. 2). The same results are obtained with the other indices that distinguish the positional isomers such as  ${}^4X_p$ ,  ${}^5X_p$  and  ${}^6X_p$  (Table II).

This method was also applied to the retention indices [16] on a squalane stationary phase for 24 methylalkane isomers with  $C_{10}$ - $C_{14}$  alkyl chains. The results were almost the same as those for alkylbenzene isomers. The correlation of  $I_{squalane}$  with  ${}^7X_p^*$  is excellent ( $r=0.9999$ ). Hence it seems that this method can be used in a general way.

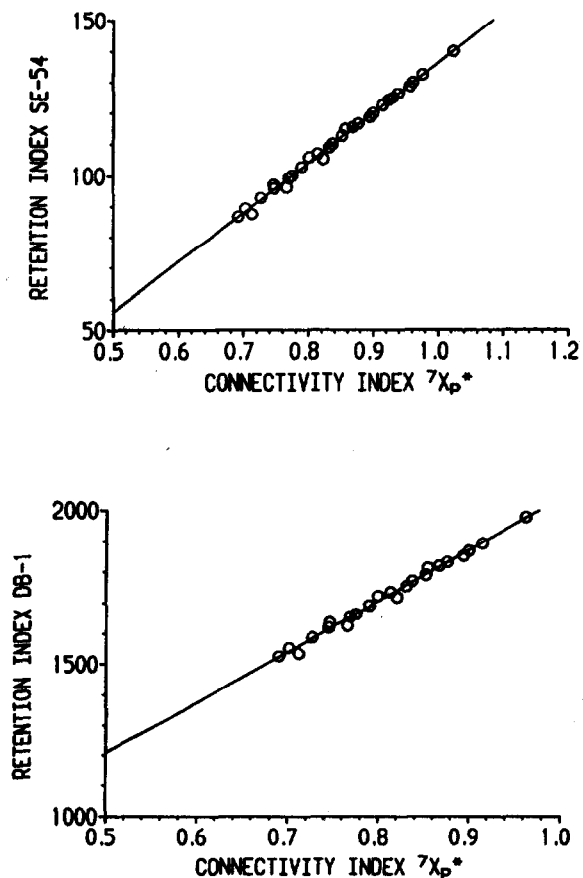


Fig. 2. Correlation between experimental retention indices (SE-54 and DB-1) and corrected molecular connectivity index  ${}^7X_p^*$  of linear alkylbenzene isomers.

TABLE II

CORRECTED VALUES OF MOLECULAR CONNECTIVITY INDICES OF LINEAR ALKYL BENZENES WITH C<sub>10</sub>-C<sub>14</sub> LINEAR ALKYL CHAINS

| Compound | <sup>4</sup> X <sub>p</sub> <sup>a</sup> | <sup>5</sup> X <sub>p</sub> <sup>a</sup> | <sup>6</sup> X <sub>p</sub> <sup>a</sup> | <sup>7</sup> X <sub>p</sub> <sup>a</sup> | <sup>4</sup> X <sub>p</sub> <sup>b</sup> | <sup>5</sup> X <sub>p</sub> <sup>b</sup> | <sup>6</sup> X <sub>p</sub> <sup>b</sup> | <sup>7</sup> X <sub>p</sub> <sup>b</sup> |
|----------|--|--|--|--|--|--|--|--|
| 1C10     | 3.0427                                   | 2.2077                                   | 1.1840                                   | 0.7747                                   | 3.0427                                   | 2.2077                                   | 1.1840                                   | 0.7747                                   |
| 2C10     | 2.9090                                   | 2.1115                                   | 1.1189                                   | 0.7268                                   | 2.9023                                   | 2.1073                                   | 1.1168                                   | 0.7271                                   |
| 3C10     | 2.8429                                   | 2.0656                                   | 1.0865                                   | 0.7026                                   | 2.8375                                   | 2.0612                                   | 1.0861                                   | 0.7015                                   |
| 4C10     | 2.8052                                   | 2.0387                                   | 1.0627                                   | 0.7131                                   | 2.8022                                   | 2.0359                                   | 1.0637                                   | 0.7123                                   |
| 5C10     | 2.7854                                   | 2.0170                                   | 1.0869                                   | 0.6916                                   | 2.7837                                   | 2.0156                                   | 1.0870                                   | 0.6903                                   |
| 1C11     | 3.2195                                   | 2.3327                                   | 1.2724                                   | 0.8372                                   | 3.2195                                   | 2.3327                                   | 1.2724                                   | 0.8372                                   |
| 2C11     | 3.0858                                   | 2.2368                                   | 1.2072                                   | 0.7893                                   | 3.0791                                   | 2.2326                                   | 1.2052                                   | 0.7896                                   |
| 3C11     | 3.0197                                   | 2.1906                                   | 1.1749                                   | 0.7698                                   | 3.0143                                   | 2.1862                                   | 1.1745                                   | 0.7687                                   |
| 4C11     | 2.9820                                   | 2.1637                                   | 1.1578                                   | 0.7469                                   | 2.9790                                   | 2.1609                                   | 1.1580                                   | 0.7461                                   |
| 5C11     | 2.9621                                   | 2.1515                                   | 1.1346                                   | 0.7670                                   | 2.9604                                   | 2.1501                                   | 1.1347                                   | 0.7657                                   |
| 6C11     | 2.9505                                   | 2.1346                                   | 1.1672                                   | 0.7476                                   | 2.9492                                   | 2.1339                                   | 1.1659                                   | 0.7452                                   |
| 1C12     | 3.3963                                   | 2.4577                                   | 1.3608                                   | 0.8997                                   | 3.3963                                   | 2.4577                                   | 1.3608                                   | 0.8997                                   |
| 2C12     | 3.2626                                   | 2.3618                                   | 1.2955                                   | 0.8518                                   | 3.2559                                   | 2.3576                                   | 1.2935                                   | 0.8521                                   |
| 3C12     | 3.1965                                   | 2.3156                                   | 1.2633                                   | 0.8323                                   | 3.1911                                   | 2.3112                                   | 1.2629                                   | 0.8312                                   |
| 4C12     | 3.1588                                   | 2.2887                                   | 1.2462                                   | 0.8141                                   | 3.1558                                   | 2.2859                                   | 1.2472                                   | 0.8133                                   |
| 5C12     | 3.1389                                   | 2.2765                                   | 1.2297                                   | 0.8008                                   | 3.1372                                   | 2.2751                                   | 1.2298                                   | 0.7995                                   |
| 6C12     | 3.1272                                   | 2.2691                                   | 1.2149                                   | 0.8230                                   | 3.1259                                   | 2.2684                                   | 1.2136                                   | 0.8206                                   |
| 1C13     | 3.5730                                   | 2.5827                                   | 1.4492                                   | 0.9622                                   | 3.5730                                   | 2.5827                                   | 1.4492                                   | 0.9622                                   |
| 2C13     | 3.4394                                   | 2.4868                                   | 1.3839                                   | 0.9143                                   | 3.4327                                   | 2.4826                                   | 1.3819                                   | 0.9146                                   |
| 3C13     | 3.3732                                   | 2.4406                                   | 1.3517                                   | 0.8948                                   | 3.3678                                   | 2.4362                                   | 1.3513                                   | 0.8937                                   |
| 4C13     | 3.3355                                   | 2.4137                                   | 1.3346                                   | 0.8766                                   | 3.3325                                   | 2.4109                                   | 1.3356                                   | 0.8758                                   |
| 5C13     | 3.3157                                   | 2.4015                                   | 1.3181                                   | 0.8681                                   | 3.3140                                   | 2.4001                                   | 1.3182                                   | 0.8668                                   |
| 6C13     | 3.3040                                   | 2.3941                                   | 1.3100                                   | 0.8568                                   | 3.3027                                   | 2.3934                                   | 1.3087                                   | 0.8544                                   |
| 1C14     | 3.7498                                   | 2.7077                                   | 1.5376                                   | 1.0247                                   |  |  |  |  |
| 2C14     | 3.6162                                   | 2.6118                                   | 1.4723                                   | 0.9768                                   |  |  |  |  |
| 3C14     | 3.5500                                   | 2.5656                                   | 1.4401                                   | 0.9573                                   |  |  |  |  |
| 4C14     | 3.5123                                   | 2.5387                                   | 1.4230                                   | 0.9391                                   |  |  |  |  |
| 5C14     | 3.4925                                   | 2.5265                                   | 1.4065                                   | 0.9306                                   |  |  |  |  |
| 6C14     | 3.4808                                   | 2.5191                                   | 1.3984                                   | 0.9240                                   |  |  |  |  |

<sup>a</sup> I<sub>SE-54</sub> from ref. 12.<sup>b</sup> I<sub>DB-1</sub> from ref. 3.

### Multiple linear correlation

The analysis by the single linear regression method demonstrates that the correlation with only one connectivity index without correction is not sufficient to give a good correlation or a correct elution sequence. This led us to test multi-variable regression equations with indices that were able to give a better representation of the molecules. To select the connectivity indices, a correlation matrix between them was applied, and to define the type of function that relates the retention indices with each connectivity index the scatter plot method was used.

The best correlation with two connectivity

indices was obtained with <sup>1</sup>X and <sup>5</sup>X<sub>p</sub> (eqns. 2 and 3):

$$I_{SE-54} = 27.5536^1X - 32.1700^5X_p - 48.6688 \quad (2)$$

$$n = 29; r = 0.9955; F(^1X) = 2110.96$$

$$(P > 0.0001);$$

$$r^2 = 0.9911; F(^5X_p) = 317.00 (P > 0.0001)$$

$$I_{DB-1} = 283.0253^1X - 329.4509^5X_p + 133.9781 \quad (3)$$

$$n = 23; r = 0.9923; F(^1X) = 1133.88$$

( $P > 0.0001$ );

$$r^2 = 0.9847; F(^5X_p) = 212.88 (P > 0.0001)$$

The  $^1X$  index conveys more information about the number of atoms in a molecule and the  $^5X_p$  index encodes more information about branching. The  $^1X$  index decreases with displacement of the phenyl group from the end to the middle of the alkyl chain of an isomeric series according to the  $I$  values, but it does not distinguish the isomers 3C, 4C, 5C and 6C. The  $^5X_p$  index increases with displacement of the phenyl group from the end to the middle of the alkyl chain and distinguishes all the compounds.

In spite of the good correlation coefficient that eqn. 2 shows, the elution sequence is not correct for eight compounds and eqn. 3 for six compounds. A better correlation is obtained with three connectivity indices  $^1X$ ,  $^3X_p$  and  $^5X_p$  (eqns. 4 and 5):

$$I_{SE-54} = 31.8111^1X - 10.5633^3X_p - 28.3486^5X_p - 4.9117 \quad (4)$$

$$n = 29; r = 0.9985; F(^1X) = 1996.83$$

( $P > 0.0001$ );

$$r^2 = 0.9969; F(^3X_p) = 47.89 (P > 0.0001);$$

$$F(^5X_p) = 546.91 (P > 0.0001)$$

$$I_{DB-1} = 331.3419^1X - 121.1496^3X_p - 285.4131^5X + 180.7905 \quad (5)$$

$$n = 23; r = 0.9979; F(^1X) = 1622.25$$

( $P > 0.0001$ );

$$r^2 = 0.9958; F(^3X_p) = 49.59 (P > 0.0001);$$

$$F(^5X_p) = 433.82 (P > 0.0001)$$

Surprisingly, the  $^3X_p$  index, which gives more information about branching in simpler molecules, permits the elution sequence of more compounds to be determined (the sequence given by eqn. 4 is wrong for only four compounds, 6C11-6C14, and that given by eqn. 5 for three compounds, 6C11-6C13).

These correlations show that the combination of different connectivity indices that encode complementary information permits the structures of the positional isomers to be distinguished and the correct elution sequence of most of them to be determined.

## CONCLUSIONS

LAB isomers with the phenyl group attached at the extremity of the alkyl chains, have a larger surface for interaction with the stationary phase, thus showing larger  $I$  values than when the phenyl group is attached in a more internal position because the molecule becomes more compact and symmetrical. While the retention index decreases with displacement of the phenyl group from the end to the middle of the alkyl chain, the connectivity indices  $^4X_p$ ,  $^5X_p$ ,  $^6X_p$  and  $^7X_p$ , which distinguish the isomers, in general increase owing to the increase in the number of subgraphs.

Thus, a single connectivity index does not show a good correlation with the retention index of positional isomers for both sets of retention indices determined with different standards, different constants assigned for each carbon atom increment and different stationary phases. Steric and conformational effects are not considered by these indices. However, compounds with a phenyl group attached in the same position of the alkyl chain of the homologous series (C10-C14) give a good correlation.

Considering the difference between the values of the intercepts on the abscissa for different homologous series, as a measure of steric effects that are not considered by the subgraphs used to calculate the connectivity indices, and assuming that all the straight lines should have the same slope, it is possible to correct the connectivity indices. Taking the difference between the  $x$  intercept of each straight line and the  $x$  intercept of the straight line for 1C10-1C14, and decreasing the values of the respective  $^7X_p$ , new values are obtained,  $^7X_p^*$ .

The new corrected molecular connectivity index was also applied to isomers of methylalkanes (with C<sub>10</sub>-C<sub>14</sub> alkyl chains) and correlated in an excellent way with the retention index

having a correct elution sequence, showing that this method could be extended to all the positional isomers of alkanes.

Multiple regression equations with different connectivity indices ( $^1X$ ,  $^3X_p$  and  $^5X_p$ ) gave very good results, showing that also using indices that encode complementary information it is possible to distinguish the structures of positional isomers and to determine the elution sequence of most of them.

#### ACKNOWLEDGEMENT

The authors thank CNPq (Brazil) for financial support.

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