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Relationship between gas chromatographic retention indices and molecular connectivity indices of chlorinated pesticides and structurally related compounds

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ABSTRACT

The ability of the molecular connectivity model to predict retention indices using both statistical correlation coefficients and correctly predicted elution sequences as criteria of fitness was tested. The tests were performed with chlorinated pesticides and some structurally related compounds. The effect on the retention index of increasing replacement by chlorine of hydrogen atoms bonded to one carbon of the aliphatic part of the molecule was excellently correlated by $^1\chi^v$, the first-order valence molecular connectivity index, using a quadratic polynomial equation. This equation also fits $^1\chi^v$ with the retention indices of halobenzenes and halobiphenyl compounds. On the other hand, $^1\chi^v$ was the most significant connectivity index, using a single linear regression equation to correlate the retention indices of all the compounds. However, $^1\chi^v$ alone was not sufficient to distinguish significantly some isomers and the correct elution sequence giving a relatively low correlation coefficient. Therefore, other connectivity indices and the consequent use of multiple linear regression equations were necessary in order to represent more completely the molecules and to obtain more accurate results.

INTRODUCTION

Studies of topological indices, such as molecular connectivity indices, were first introduced by Randic [1] and were further developed and extensively used by Kier [2]. This method gives a quantitative description of the molecular structure by attributing numerical values to the atoms. The importance of this method was demonstrated by the excellent correlations obtained between the theoretical indices and the experimental values of physico-chemical properties [3–5], biological activity [6–9] and chromatographic retention indices [10–14].

Correlations of chromatographic retention with the physico-chemical and structural characteristics of substances are the basis for the choice of appropriate chromatographic systems and are of great significance for solving problems involving the identification of components of complex mixtures, *e.g.*, giving supplementary information to gas chromatographic–mass spectrometric results for the identification of individual components.

The correlation between the retention indices and the structural parameters is based on the assumption of additivity of the free energies of interaction of the sorbates with the stationary phase, which may be calculated by adding up the structural parts of the molecule.

This work was carried out in order to test the ability of connectivity indices to predict the retention indices, on polar and non-polar stationary phases, of DDT and related compounds. These compounds were selected because they and other chlorinated benzenes and hydrocarbons constitute an important group of environmentally hazardous compounds, because they provide a challenge to the molecular connectivity model owing to the effect of chlorine substitution (shown by Haken and Korhonen [15] to be non-linear) and because of the complexity of their molecular structures.

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Sabljic [16] showed that frequently the criterion used to test the fitness between the observed and calculated retention indices in investigations is the statistical correlation coefficient. This criterion is insufficient to test the usefulness of the topological approach for predicting retention indices, as a high correlation coefficient does not necessarily imply a correct elution sequence. Hence a high correlation coefficient and a correctly predicted elution sequence are prerequisites for the prediction of retention indices.

These aspects were examined in order to find the best linear regression equation and molecular connectivity parameters to permit the prediction of the gas chromatographic retention indices of the compounds studied.

EXPERIMENTAL

Method of calculation

The molecular connectivity indices used were $^1\chi$, $^1\chi^v$, $^3\chi_p$, $^3\chi_c$, $^3\chi_c^v$, $^4\chi_{pc}$ and $^4\chi_{pc}^v$, which were calculated according to Kier [1].

The compounds used were 1,1-diphenylethane (DDO_H), 1,1-bis(4-chlorophenyl)ethane (DDO), 1,1-bis(4-chlorophenyl)-2-chloroethane (DDM), 1, 1-diphenyl-2,2-dichloroethane (DDD_H), 1,1-bis(4-methylphenyl)-2,2-dichloroethane (DDD_{CH_3}), 1,1-bis(4-ethylphenyl)-2,2-dichloroethane ($DDD_{C_2H_5}$), 1-(2-chlorophenyl)-1-(4-chlorophenyl)-2,2-dichloroethane ($DDD_{o,p'\text{-Cl}}$), 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (DDD), 1,1-bis(4-methoxyphenyl)-2,2-dichloroethane (DDD_{OCH_3}), 1,1-bis(4-bromophenyl)-2,2-dichloroethane (DDD_{Br}), 2,2-diphenyl-1,1,1-trichloroethane (DDT_H), 2,2-bis(4-methylphenyl)-1,1,1-trichloroethane (DDT_{CH_3}), 2-(2-chlorophenyl)-2-(4-chlorophenyl)-1,1,1-trichloroethane ($DDT_{o,p'\text{-Cl}}$), 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT), 2,2-bis(4-hydroxyphenyl)-1,1,1-trichloroethane (DDT_{OH}), 1,2-bis(4-chlorophenyl)-1-chloroethane (DDMF), 2,2-bis(4-chlorophenyl) ethanoic acid (DDA), 1,1-bis(4-chlorophenyl)-2-hydroxyethane (DDOH), 1,1-diphenyl-2-chloroethylene ($DDMU_H$), 1,1-bis(4-chlorophenyl)-2-chloroethylene(DDMU), 1,1-diphenylethylene ($DDNU_H$), 1,1-bis(4-chlorophenyl)ethylene (DDNU), 1,1-diphenyl-2,2-dichloroethylene (DDE_H), 1,1-bis(4-methylphenyl)-2,2-dichloroethylene(DDE_{CH_3}), 1-(2-chlorophenyl)-1-(4-chlorophenyl)-2,2-dichloroethylene ($DDE_{o,p'\text{-Cl}}$), 1,1-bis(4-chlorophenyl)-2,2-dichloroethylene (DDE), 1,1-bis(4-methoxyphenyl)-2,2-dichloroethylene (DDE_{OCH_3}), 1,2-diphenylethylene (DCS_H), 1,2-bis(4-methylphenyl)ethylene (DCS_{CH_3}) and 1,2-bis(4-chlorophenyl)ethylene (DCS).

The retention indices (I) of the above compound were reported by Zanette [17] and were obtained using a nickel column (5.5 m × 3.2 mm I.D.) and a glass column (1.8 m × 3.2 mm I.D.) packed with 3% OV-17 on Chromosorb W AW DMCS (80–100 mesh) as a polar stationary phase and a glass column (1.8 m × 3.2 mm I.D.) with 15% Apiezon L (ApL) on Chromosorb W as a non-polar stationary phase, with a column temperature of 215°C.

All calculations in single and multiple linear regression analyses were carried out on an IBM PC/XT computer.

RESULTS AND DISCUSSION

Study of the additivity of the effect of the increase in chlorine substitution

The effect of multiple chlorine replacement of hydrogen atoms was first studied considering the compounds containing one, two or three chlorine atoms bonded to one carbon of the aliphatic part of the molecule. The $^1\chi$ and $^1\chi^v$ connectivity indices give a good linear correlation (eqn. 1) and a correct elution sequence. The correlation coefficients are indicated in Table I.

$$I_i = A + B\chi_i \quad (1)$$

In spite of this good correlation, the increase in the retention indices with increase in the number of chlorine atoms showed that the values were not additive. For this reason, the experimental values of I were tested using other equations, and the best results, with both polar and non-polar phases, were obtained with the quadratic polynomial equation

$$I_i = A + B\chi_i + C(\chi_i)^2 \quad (2)$$

It is interesting that for groups of compounds with increasing chlorine substitution on the aliphatic carbon, but with some structural differences, such as DDO, DDM, DDD and DDT with respect to DDO_H, DDM_H, DDD_H and DDT_H, when the retention indices corresponding to each group are correlated with $^1\chi^v$ by the quadratic polynomial eqn.

TABLE I

EFFECT OF CHLORINE SUBSTITUTION ON THE RETENTION INDICES OF PESTICIDES AND THEIR CORRELATION WITH CONNECTIVITY INDICES

Compounds	Linear equation	Quadratic polynomial equation	Stationary phase
DDO, DDM, DDD, DDT	$I = 286.0699\,^1\chi - 213.6038$ $n = 4, r = 0.9654, r^2 = 0.9320$	$I = 3776.687\,^1\chi - 211.4237\,(^1\chi)^2 - 14576.87$ $n = 4, r = 0.9987, r^2 = 0.9974$	ApL
	$I = 373.1168\,^1\chi - 644.9431$ $n = 4, r = 0.9810, r^2 = 0.9623$	$I = 3767.867\,^1\chi - 205.6175\,(^1\chi)^2 - 14613.7$ $n = 4, r = 0.9999, r^2 = 0.9998$	OV-17
	$I = 231.0055\,^1\chi^v + 591.7717$ $n = 4, r = 0.9672, r^2 = 0.9355$	$I = 2032.495\,^1\chi^v - 133.8105\,(^1\chi^v)^2 - 5428.305$ $n = 4, r = 0.9999, r^2 = 0.9998$	ApL
	$I = 310.1502\,^1\chi^v + 406.4995$ $n = 4, r = 0.9823, r^2 = 0.9649$	$I = 2042.253\,^1\chi^v - 129.3253\,(^1\chi^v)^2 - 5411.773$ $n = 4, r = 0.9999, r^2 = 0.9998$	OV-17
DDO_H, DDM_H, DDD_H, DDT_H	$I = 250.4838\,^1\chi - 94.3365$ $n = 4, r = 0.9968, r^2 = 0.9937$	$I = 964.4149\,^1\chi - 47.7967\,(^1\chi^v)^2 - 2750.295$ $n = 4, r = 0.9991, r^2 = 0.9982$	ApL
	$I = 395.1449\,^1\chi - 938.9389$ $n = 4, r = 0.9848, r^2 = 0.9698$	$I = 3305.604\,^1\chi - 194.8507\,(^1\chi^v)^2 - 11766.44$ $n = 4, r = 0.9999, r^2 = 0.9999$	OV-17
	$I = 210.5761\,^1\chi^v + 624.6025$ $n = 4, r = 0.9972, r^2 = 0.9943$	$I = 531.5087\,^1\chi^v - 28.8874\,(^1\chi^v)^2 - 308.1047$ $n = 4, r = 0.9992, r^2 = 0.9984$	ApL
	$I = 318.146\,^1\chi^v + 194.3096$ $n = 4, r = 0.9856, r^2 = 0.9713$	$I = 1721.411\,^1\chi^v - 122.863\,(^1\chi^v)^2 - 3772.679$ $n = 4, r = 0.9999, r^2 = 0.9999$	OV-17
DDO, DDM, DDD, DDT, DDO_H, DDM_H, DDD_H, DDT_H	$I = 357.6265\,^1\chi - 855.8640$ $n = 8, r = 0.9545, r^2 = 0.9107$	$I = 143.358\,^1\chi - 13.5728\,(^1\chi)^2 - 15.1131$ $n = 8, r = 0.9546, r^2 = 0.9107$	ApL
	$I = 449.4493\,^1\chi - 1314.5$ $n = 8, r = 0.9793, r^2 = 0.9590$	$I = 969.4059\,^1\chi - 32.9382\,(^1\chi)^2 - 3354.61$ $n = 8, r = 0.9803, r^2 = 0.9610$	OV-17
	$I = 284.1314\,^1\chi^v + 187.317$ $n = 8, r = 0.9607, r^2 = 0.9229$	$I = 166.5885\,^1\chi^v - 9.3840\,(^1\chi^v)^2 - 549.9678$ $n = 8, r = 0.9612, r^2 = 0.9240$	ApL
	$I = 355.8\,^1\chi^v + 4.3818$ $n = 8, r = 0.9833, r^2 = 0.9668$	$I = 600.2858\,^1\chi^v - 19.4215\,(^1\chi^v)^2 - 725.309$ $n = 8, r = 0.9843, r^2 = 0.9690$	OV-17

2, excellent correlation coefficients are obtained (Table I). However, when the two groups are considered together, the correlation coefficient is smaller because each group clearly follows a separate distinct curve, as can be seen in Fig. 1.

A lack of additivity is observed for the increase in the retention indices produced by chlorine substitutions on the aromatic ring (mono-, di-, tri-, tetra-, penta- and hexachlorobenzenes) according to the values given by Sabljic [18].

The correlations were also done with the retention values given by Hasan and Jurs [19] for polyhalogenated biphenyls. The compounds utilized were those with one or more chlorine atoms as substituents on one of the aromatic rings, such as 2-chlorobiphenyl, 2,3-dichlorobiphenyl, 2,3,4-trichlorobiphenyl, 2,3,4,5-tetrachlorobiphenyl, or on both of the aromatic rings, such as decachlorobiphenyl. The best results are observed when the quadratic polynomial equation is used (Table II).

Correlation between chromatographic retention indices and connectivity indices for all compounds

Different molecular connectivity indices and experimental retention indices of the 30 compounds examined are shown in Table II.

The best correlation of the retention indices on both stationary phases (ApL and OV-17) was ob-

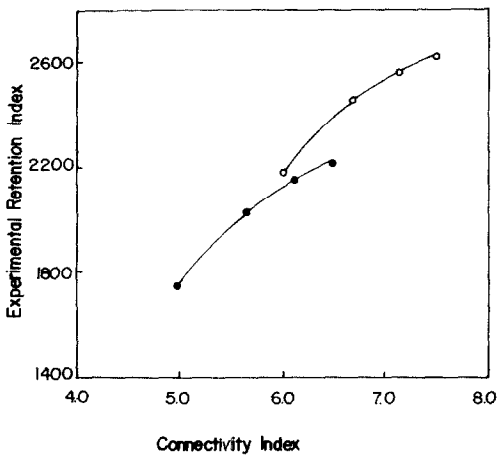

Fig. 1. Correlation between experimental retention indices (polar stationary phase, OV-17) and molecular connectivity index $^1\chi^v$ by the quadratic polynomial eqn. 2. ○ = DDO, DDM, DDD and DDT; ● = DDO_H, DDM_H, DDD_H and DDT_H.

tained using the one-variable eqn. 1 with the first-order and valence first-order molecular connectivity indices, $^1\chi$ and $^1\chi^v$.

The $^1\chi^v$ index is more selective than $^1\chi$, considering that it distinguishes the degree of unsaturation and the presence of heteroatoms. Thus, $^1\chi$ (as $^3\chi_p$, $^3\chi_c$ and $^4\chi_{pc}$) cannot distinguish between a group of six compounds, three groups of three compounds and five groups of two compounds, whereas $^1\chi^v$ indices cannot distinguish significantly only between the isomers $DDE_{o,p\text{-Cl}}$ and DDE, $DDD_{o,p'\text{-Cl}}$ and DDD and $DDT_{o,p'\text{-Cl}}$ and DDT (Table III).

For the *I* value of the 30 compounds on OV-17, the correlation coefficient with $^1\chi^v$ was 0.8393 and with $^1\chi$ 0.8599. For the *I* value of 23 compounds for which experimental determinations exist, on the non-polar stationary phase (ApL) the correlation coefficient with $^1\chi^v$ was 0.8071 and on the polar stationary phase (OV-17) it was 0.8454. Figs. 2 and 3 show the plots of *I* as a function of $^1\chi^v$ on the two stationary phases. The correlation coefficients are relatively low. However, the *t*-test (90% confidence) is significant.

Correlation between retention indices on a polar phase (OV-17) and a single connectivity index

The compounds that have a larger dispersion on the polar stationary phase (OV-17) with the connectivity index ($^1\chi^v$) are DDT_{OH}, DDD_{OH}, $DDD_{C_2H_5}$, DDA, DDE_{OCH_3}, DDD_{OCH_3} and DCS (Fig. 1).

For $DDD_{C_2H_5}$, the value of the $^1\chi^v$ increases significantly relative to that of DDD owing to the larger numbers of substructures by the addition of

TABLE II

EFFECT OF CHLORINE SUBSTITUTION ON THE RETENTION INDICES OF BENZENE AND BIPHENYL AND THEIR CORRELATION WITH CONNECTIVITY INDICES

Compounds	Linear equation	Quadratic polynomial equation	Stationary phase[a]
Mono-, 1,2-di-, 1,2,3-tri, 1,2,3,4-tetra-, penta-, hexachlorobenzene	$I = 421.3038^1\chi - 61.6637$ $n = 6, r = 0.9849, r^2 = 0.9700$	$I = 1366.585^1\chi - 106.7444\ (^1\chi)^2 - 2101.229$ $n = 6, r = 0.9965, r^2 = 0.9930$	C-20M
	$I = 418.4995^1\chi - 545.593$ $n = 6, r = 0.9973, r^2 = 0.9945$	$I = 833.3634^1\chi - 46.8479\ (^1\chi)^2 - 1440.71$ $n = 6, r = 0.9995, r^2 = 0.9990$	SE-30
	$I = 337.9849^1\chi^v + 519.3046$ $n = 6, r = 0.9853, r^2 = 0.9707$	$I = 851.1492^1\chi^v - 67.5898\ (^1\chi^v)^2 - 402.3637$ $n = 6, r = 0.9965, r^2 = 0.9930$	C-20M
	$I = 335.67^1\chi^v + 31.7508$ $n = 6, r = 0.9974, r^2 = 0.9949$	$I = 553.687^1\chi^v - 28.7154\ (^1\chi^v)^2 - 359.8143$ $n = 6, r = 0.9995, r^2 = 0.9990$	SE-30
2-Chlorobiphenyl, 2,3-di-, 2,3,4-tri-, 2,3,4,5-tetra-, decachlorobiphenyl	$I = 324.2829^1\chi^v + 283.1577$ $n = 5, r = 0.9969, r^2 = 0.9938$	$I = 546.4355^1\chi^v - 15.7442\ (^1\chi^v)^2 - 447.2039$ $n = 5, r = 0.9985, r^2 = 0.9970$	DB-210-CB

[a] C-20M = Carbowax 20M polar stationary phase; SE-30 = non-polar stationary phase; DB-210-CB = polar stationary phase (capillary column).

TABLE III

MOLECULAR CONNECTIVITY INDICES AND OBSERVED RETENTION INDICES OF PESTICIDES AND RELATED COMPOUNDS ON NON-POLAR (APIEZON L) AND POLAR (OV-17) STATIONARY PHASES AT 215°C

Compound	$^1\chi$	$^1\chi^v$	$^3\chi_p$	$^3\chi_c$	$^3\chi_c^v$	$^4\chi_{pc}$	$^4\chi_{pc}^v$	I^a	
								ApL	OV-17
DDO_H	6.8760	4.9750	4.7860	0.5258	0.3368	1.5400	0.8430	1620	1750
DDO	7.6620	5.9970	5.6080	1.1032	0.7352	2.3560	1.3030	1950	2184
DDM	8.2000	6.6730	5.8030	1.0469	0.6930	2.2360	1.2720	2168	2460
DDD_H	7.7860	6.1100	5.1570	0.7777	0.7520	1.7780	1.2960	1854	2156
DDD_{CH_3}	8.5720	6.9340	5.9790	1.3551	1.0854	2.5940	1.6810	–	2335
$DDD_{C_2H_5}$	9.6500	8.0540	6.7880	1.1859	0.9877	2.7630	1.8040	2232	2524
$DDD_{o,p'\text{-Cl}}$	8.5880	7.1340	6.0440	1.2716	1.1108	2.6980	1.8900	2184	2502
DDD	8.5720	7.1320	5.9790	1.3551	1.1504	2.5940	1.7560	2272	2572
DDD_{OCH_2}	9.6500	7.1580	6.7880	1.1859	0.8881	2.7630	1.5890	–	2775
DDD_{Br}	8.5720	7.9330	5.9790	1.0664	1.4187	2.5940	2.0660	–	2820
DDT_H	8.0870	6.4800	5.3140	1.5069	1.9432	2.0580	1.6650	1926	2224
DDT_{CH_3}	8.8740	7.3040	6.1360	2.0843	2.2770	2.8740	2.0500	2124	2436
$DDT_{o,p'\text{-Cl}}$	8.8910	7.5060	6.2070	2.1694	2.3019	2.9820	2.2600	–	2563
DDT	8.8740	7.5000	6.1340	2.0843	2.3416	2.8740	2.1250	2284	2632
DDT_{OH}	8.8740	6.7540	6.1360	2.0843	2.0923	2.8740	1.8360	–	2783
DDMF	8.1440	6.5830	5.7050	1.1839	0.8565	2.2130	1.3620	2196	2400
DDA	8.5720	6.1340	5.9790	1.3551	0.7158	2.5940	1.1560	1933	2475
DDOH	8.2000	6.1430	5.8030	1.0468	0.6930	2.2360	1.1960	2186	2517
$DDMU_H$	7.4140	5.2990	4.9810	0.4694	0.1555	1.4200	0.6240	1704	1960
DDMU	8.2000	6.3190	5.8030	1.0468	0.6372	2.2360	1.0850	2132	2384
$DDNU_H$	6.8760	4.6740	4.7860	0.5258	0.2550	1.5400	0.5970	1634	1760
DDNU	7.6620	5.6940	5.6080	1.1032	0.6534	2.3560	1.0580	1972	2166
DDE_H	7.7860	5.7650	5.1570	0.7777	0.5862	1.7780	1.0090	1754	2062
DDE_{CH_3}	8.5720	6.5900	5.9790	1.3551	0.7526	2.5940	1.3940	1974	2274
$DDE_{o,p'\text{-Cl}}$	8.5880	6.7900	6.0440	1.2716	0.9473	2.6980	1.5820	–	2396
DDE	8.5720	6.7880	5.9790	1.3551	0.9846	2.5940	1.4690	2180	2452
DDE_{OCH_3}	9.6500	6.8140	6.7880	1.1859	0.8219	2.7630	1.3020	–	2670
DCS_H	6.9480	4.7310	4.4310	0.4082	0.1925	0.8670	0.3330	1778	1972
DCS_{CH_3}	7.7340	5.5550	5.2520	0.9856	0.5258	1.6830	0.7180	2003	2177
DCS	7.7340	5.7510	5.2520	0.9856	0.5909	1.6830	0.7930	2217	2450

[a] Observed retention indices of pesticides are those reported in ref. 17.

the ethyl group to the molecule, but the increase in the experimental retention index is relatively smaller because the ethyl group is non-polar.

DCS has an experimental I value that shows a large positive deviation from the correlation line. The cause is unknown. However, the very high deviation observed also on the non-polar phase (ApL) suggests that the I value might depend strongly on the surface area and size of the molecule. It is observed that the values of the connectivity indices for DCS and DDNU, similar to those for DCS_H and $DDNU_H$, are close because the molecules have the same number of subgraphs, but the I values are different. DCS and DCS_H show larger I values than $DDNU_H$ and DDNU, possibly because in the former compounds the aromatic rings are bonded to different carbon atoms of the ethylene group, and in this way the molecule has a larger contact surface, thereby increasing the interaction with the stationary phase and consequently the retention time in the column.

The compounds that have polar groups such as the "OH" and "OCH_3" compounds show higher I values than those calculated through the connectivity index ($^1\chi^v$). This result may be due in part to the method of calculation.

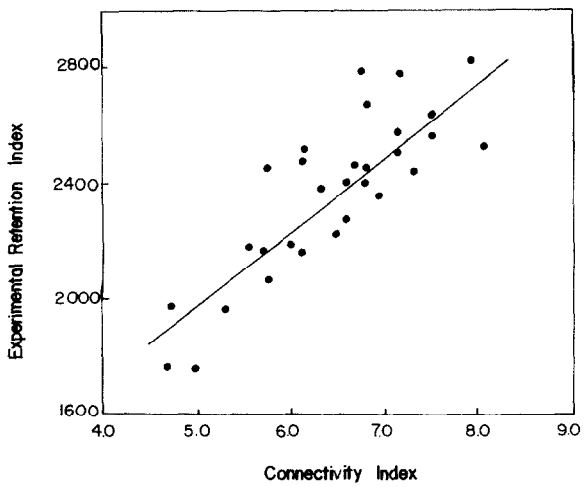

Fig. 2. Correlation between experimental retention indices (polar stationary phase, OV-17) and molecular connectivity index $^1\chi^v$ for 30 compounds.

It is known that the values of the connectivity index $^1\chi^v$ refer to subgraphs consisting of two adjacent and consecutive vertices (atoms). The vertices are described by their valence delta values (δ^v) according to the expression

$$\delta^v = Z^v - h \tag{3}$$

for atoms beyond the first row of the Periodic Table (*e.g.*, for oxygen $\delta^v = 6$), where Z^v is the number of valence electrons in the atom (vertex) and h is the number of hydrogen atoms bonded to the same atom. For atoms beyond the second row in the Periodic Table, the relationship which leads to appropriate δ^v is

$$\delta^v = \frac{Z^v - h}{Z - Z^v} \tag{4}$$

where Z is the atomic number.

The compounds studied have only chlorine and oxygen as heteroatoms in the molecule. The value of δ^v of the chlorine atom calculated through the eqn. 4 is 0.7. As this value is less than 1 it contributes to increasing the $^1\chi^v$ value, according to the increase that occurs in the experimental I value due to the presence of the polar chlorine atom.

However, with oxygen, eqn. 3 gives a value of $\delta^v = 5$ for "OH", which contributes to a decrease in the value of $^1\chi^v$, whereas the experimental I value increases in the presence of a polar OH group.

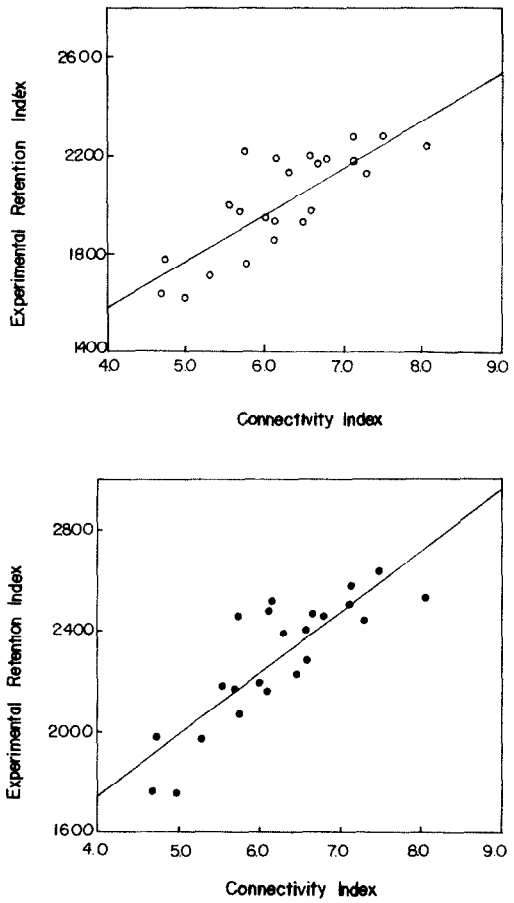

Fig. 3. Correlation between experimental retention indices and molecular connectivity index $^1\chi^v$ for 23 compounds. ○ = Non-polar stationary phase (ApL); ● = polar stationary phase (OV-17).

If eqn. 4 is utilized to calculate the value of δ^v for the oxygen atom of OH, OCH_3 and C=O groups, smaller values are obtained. In this instance, the final values of $^1\chi^v$ increase like the experimental I values. Thus, if the $^1\chi^v$ values of compounds having oxygen in the molecule (DDOH, DDA, DDT_{OH}, DDE_{OCH_3}, DDD_{OCH_3}) are calculated using eqn. 4 for δ^v of oxygen, a better correlation coefficient with the I values ($r = 0.8781$) is obtained.

Correlation between retention indices on a non-polar stationary phase (Apiezon L)

With the non-polar stationary phase ApL the

compounds that show the largest dispersion in the correlation between I and $^1\chi^v$ are DCS, DDOH, $DDD_{C_2H_5}$, DDO_H and DDE_H (Fig. 2).

The $^1\chi^v$ value of DCS (which has one chlorine atom in each aromatic ring) and DCS_{CH_3} (which has one methyl group in each aromatic ring) are very close, in spite of the consideration of the value of $\delta^v = 0.7$ for the chlorine atom and $\delta^v = 1$ for the methyl group compared with the difference existing between the values of the retention indices.

For compounds with polar groups such as OH and OCH_3, the same results as for the polar phase (OV-17) were obtained.

Correlation between chromatographic retention indices and connectivity indices by multiple linear correlation equations

The analyses by the single linear regression method demonstrate that correlations with only one variable are not sufficient to discriminate clearly the compounds or their 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. From this exploratory data analysis we selected as independent variables $^1\chi$ or $^1\chi^v$; $^3\chi_p$; $^3\chi_c$ or $^3\chi_c^v$; and $^4\chi_{pc}$ or $^4\chi_{pc}^v$.

In spite of the fact that the best correlation coefficient with two variables was obtained with $^1\chi$ and $^3\chi_c$ ($r = 0.8909$), the best result with two-variable equations was obtained with $^1\chi^v$ and $^3\chi_p$ ($r = 0.8729$), considering that these last two variables are able to distinguish significantly all the compounds (see eqns. 5, 6 and 7).

$$I = 265.4079\,{}^1\chi^v + 652.0186 \qquad (5)$$

$r = 0.8393 \qquad F = 66.70 \qquad (P > 0.0001)$

where P is the level of probability indicated by the sample;

$$I = 244.2217\,{}^1\chi + 177.3415\,{}^3\chi_c + 120.8026 \qquad (6)$$

$r = 0.8909 \qquad F(^1\chi) = 31.87 \qquad (P > 0.0001)$

$\qquad\qquad F(^3\chi_c) = 7.11 \qquad (P > 0.0128)$

$$I = 133.80\,{}^1\chi^v + 229.20\,{}^3\chi_p + 182.80 \qquad (7)$$

$r = 0.8729 \qquad F(^1\chi^v) = 79.88 \qquad (P > 0.0001)$

$\qquad\qquad F(^3\chi_p) = 6.55 \qquad (P > 0.0166)$

The correlation coefficient is better than with a single linear regression equation ($^1\chi^v$) owing the existence of other factors besides correspondence with $^1\chi^v$ (which distinguish the degree of unsaturation and the presence of heteroatoms) participating in the physico-chemical process of retention of the compounds. In this case, $^3\chi_p$ is a topological description that includes the size and degree of branching of the molecules.

Equations with three or more connectivity indices show that the third or fourth variables do not meet the 0.15 significance level for entry into the statistical analysis model.

CONCLUSIONS

The increase in the values of the retention indices with increase in the number of chlorine atoms in the molecule is non-linear. The correlation by a single linear regression equation of the retention indices and the molecular connectivity indices ($^1\chi^v$) is good because it takes only a first relatively linear part of a curve. For this reason, the correlation by a quadratic polynomial equation gives the best results with chlorinated pesticides, chlorinated aromatic compounds and halogenated biphenyls.

The molecular connectivity indices do not entirely predict, by a single linear regression equation, the chromatographic retention indices and the correct elution sequence of the different chlorinated pesticides and related compounds. Using two connectivity indices, it is possible to represent more aspects of the structure of the molecules that are important in their interaction with the stationary phase, and therefore the multiple linear regression equation gives better results.

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