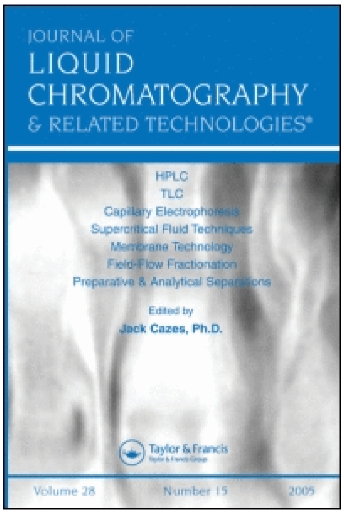

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TRIATOMIC METHOD FOR CORRELATION OF RETENTION OF POLYNUCLEAR AROMATIC HYDROCARBONS ON NORMAL PHASE HPLC

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ABSTRACT

A triatomic additivity method for correlating retention indices of polynuclear aromatic compounds on nitrogen-containing polar bonded phase in normal phase high performance liquid chromatography is described. The method of trigonal additivity shows good correlation with all the four amino bonded phases studied and compares favorably with the well known connectivity index of Randic.

INTRODUCTION

Polynuclear aromatic compounds (PNAs) are ubiquitous compounds which have been established as priority pollutants by the Environmental Protection Agency. These compounds have been the subject of extensive and intensive research. In

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particular, the use of amino bonded phase packing materials in high performance liquid chromatography (HPLC) as part of a scheme for the separation of PNAs in complex samples has been actively investigated. The widespread use of this scheme was introduced by Wise and co-workers (1). In this procedure, the PNAs are first fractionated according to ring sizes on the amino bonded phase, using normal phase HPLC (NP-HPLC). The collected fractions are subsequently resolved into components by reversed phase HPLC (RP-HPLC). Several workers have since then demonstrated the applicability of this procedure for analysis of PNAs in diverse samples (2-4).

Wise et al. (1) have also suggested that retention on the normal phase μBondapak amine column is electronic in nature, i.e. the retention is a function of the interaction between the aromatic π electrons of the PNAs and the polar amino group of the stationary phase. Therefore, alkyl substituents on the PNAs do not significantly affect the retention as the alkyl groups exert negligible influence on the π system. Hence, separation by ring size is observed. Boduszynski et al. (4), in their analysis of coal liquids by this methodology, confirmed that the elution profile on the amino bonded phase correlated well with the number of double bonds, i.e. ring size of PNAs. Karlesky et al. (5) have demonstrated that the charge-transfer mechanism is the most plausible.

Indeed, retention characteristics in HPLC using chemically bonded phases has been an intriguing subject. Numerous workers have worked with different packing materials and have attempted to elucidate their retention characteristics (6-12). Colin and Guiochon (13) have given a concise review of the topic for RP-HPLC.

Another approach to studying the retention properties of chemically-bonded phase liquid chromatography is to correlate experimentally determined retention indices with reasonable physicochemical parameters. From such exercises, deductions and inferences on the kinds of interactions responsible for retention may be drawn. Better yet, the model can gain more credence if its predictive power can be demonstrated. Many workers have attempted this for RV-HPLC. For instance, Streuli and Orloff (14) correlated the chromatographic adsorption constants on Sephadex LH-20 Dextran of aromatic compounds with their delocalization energies. They obtained good correlation with different classes of compounds. However, there were always exceptions in each class. They found that it is not the capability of using such correlation to quantitatively distinguish between all the individual compounds that is necessarily of prime importance, rather, from such results one should gain an understanding of the relative importance of the different factors in determining the retention characteristics. Wise and co-workers (15) had shown that the length-to-breadth ratio of PNAs correlated well with retention data on C-18 RV-HPLC. Jandera et al. (16) developed the interaction indices for the prediction of retention. Hanai and Hubert (17) explored the influence of Van der Waals volumes and the π energy of molecules on RP-HPLC retention. Jinno and Kawasaki (18) studied several descriptors in RV-HPLC and observed their correlation with retention data of PNAs, both individually and when the descriptors were combined in a multiparameter correlation. Hasan and Jurs (19), besides presenting their own findings using multiple factors, also gave a succinct account of many of the important publications on this subject.

However, in NP-HPLC, for nitrogen-containing chemically-bonded phases, although applications, selectivity and retention characteristics have been studied (1,4,11,12,20,21) no extensive studies, as those that have been done for RV-HPLC, on correlations between retention and physico-chemical properties of molecules have been carried out. Eknig et al. (22) did perform a study on perfluorocarbon modified silica gel and found a linear correlation between retention and resonance energy of the PNAs. Boduszynski et al. (4) correlated the number of double bonds with retention for the amino bonded phase NP-HPLC.

In this paper, we remedy this deficiency by introducing a new method, trigonal additivity, for correlating retention indices in the use of polar bonded phase NP-HPLC. The method is based on trigonal additivity (22) as a means to quantitatively assign values for the structural, and more importantly, electronic properties of PNAs, and to correlate these values with their retention indices on nitrogen-containing bonded phases in NP-HPLC. Trigonal additivity was first introduced by Somayajulu and Zwolinski to correlate thermodynamic properties of alkanes (23) and PNAs (22). Their method has as its basis, Brown's model for quantum mechanical calculation of the electronic energies of alkane (25). Trigonal additivity thus takes into consideration all of the major electronic interactions of the molecules. Since it has been applied with success by Somayajulu and Zwolinski for correlating thermodynamic properties of molecules, it should be an appropriate approach for correlating retention data in chromatography. We will also present results from the well known molecular connectivity index of Randic (26,27). This is done solely for purposes of comparison and validation of our results from trigonal additivity and to offer plausible explanations for the observed correlations.

EXPERIMENTAL

Instrumentation

A Hewlet Packard (Palo Alto, CA) 9845 B desktop computer equipped with a 16.7 megabyte HP7908 disk was used for data analysis. A Basic Statistics package including a Multiple Regression program from Hewlett Packard (part #09845-15111 rev. B) was used to do the statistical analysis for predicting retention indices. A simpler Regression package was used for all other statistical analysis.

Chromatography was performed on a microprocessor controlled Altex Model 312 MP liquid chromatograph equipped with a UV detector monitoring at 254 nm. The column (30 cm x 10 mm i.d.) was packed with 10 micron particle size Chromosorb LC-9 (Supelco Inc., Belefonte, PA) which is an n-propylamine bonded stationary phase.

Reagents

All PNAs used were purchased at 95% purity or better from various suppliers and were used without further purification. Standards for all normal phase work were prepared by dissolving the appropriate amount of each standard to prepare solutions with concentrations of approximately 10^{-4} M. The mobile phase eluent was glass distilled cyclohexane (Burdick and Jackson Laboratories, Muskegon, MI).

Procedure

The PNAs were analyzed on Chromosorb LC-9 in the normal phase mode with cyclohexane as the mobile phase. The standard retention indices were assigned as follows: benzene 10, naphthalene 100, anthracene 1000, 1,2-benzanthracene 10,000 and 1,2,3,4-dibenzanthracene 100,000. The retention indices were calculated according to the equation given by Popl et al. (8). The retention indices for the PNAs obtained on this column are compared with literature values, μBondapak NH_2 (2), pyrrolidone (20) and diamine (21). These values are tabulated in Table 1. Note that the PNAs used as index compounds by previous workers (2,20,21) may not be identical. This should not be a serious concern as was discussed in our previous study (5).

THEORY

1. Molecular Connectivity Index (X). The molecular connectivity introduced by Randic (26) is a topological parameter which was designed to quantitatively characterize the degree of molecular branching. Many references on connectivity can be found in the literature (26,27,29-32). Interested readers can refer to them for calculations and application procedures using connectivity. Table 1 presents a list of PNAs used, their connectivity values and retention indices on different nitrogen-containing stationary phases.

2. Trigonal Additivity. The simplest approach to estimating a given property "P" by an additivity approach is atomic additivity. Since PNAs have the general formula C_nH_m, we may write

$$P = na_1 + ma_0 \qquad (1)$$

where a_1 is the contribution of an aromatic carbon atom, a_0 is the contribution of a hydrogen atom, n is the number of aromatic carbons and m is the number of hydrogen atoms. In this approach, it is assumed that all hydrogens and carbons make the same contribution despite their structural features.

In the bond additivity procedure, we consider the contribution of various bonds. Since there are only two types of bonds possible in PNAs, the parameter of P to be estimated is defined as

$$P = \frac{(3n - m)}{2} a_{11} + ma_{10} \qquad (2)$$

where a_{11} is the contribution of the C-C bond and a_{10} is the contribution of the C-H bond.

TABLE 1

	Compound	LC-9 Amine	Bondapak(2) Amine	Pyroll-(23) idone	Diamine(24) 100% $C_{56}H_6$	Diamine(24) 6% CH_2Cl_2	Connectivity Index
1.	Benzene	1.00	1.00	1.00	1.000	--	2.000
2.	Biphenyl	1.93	2.16	1.40	2.252	--	4.571
3.	Naphthalene	2.00	2.00	2.00	2.000	--	3.405
4.	-2-Phenyl	--	--	--	3.152	--	5.476
5.	-1,2,3,4-Tetraphenyl	--	--	--	--	4.402	11.720
6.	Acenaphthylene	2.64	2.59	2.26	3.199	--	4.149
7.	p-Terphenyl	3.28	3.28	2.88	3.490	--	6.143
8.	o-Terphenyl	--	2.50	2.57	2.731	--	6.149
9.	m-Terphenyl	--	3.12	--	3.330	--	6.143
10.	Anthracene	3.00	2.94	2.96	2.916	--	4.809
11.	-9,10-Diphenyl	--	--	3.16	3.470	--	8.765
12.	Phenanthrene	3.12	3.00	3.00	3.000	3.000	4.815
13.	Fluoranthene	3.60	3.51	3.46	3.586	--	5.565
14.	-Benzo(b)	--	4.48	--	--	4.435	6.976
15.	-Benzo(j)	--	4.56	--	--	--	6.976
16.	-Benzo(k)	--	4.45	--	--	4.435	6.970
17.	-Benzo(g,h,i)	--	3.84	--	--	--	6.309
18.	Pyrene	3.43	3.37	3.47	3.433	--	5.559
19.	Chrysene	3.87	4.01	3.83	--	4.00	6.226

20.	Naphthacene	--	3.95	--	--	--	6.214
21.	p-Quaterphenyl	4.05	4.50	3.90	--	--	8.214
22.	Triphenylene	4.23	4.07	3.91	--	4.169	6.232
23.	Benz(a)anthracene	4.00	4.00	4.00	4.000	4.000	6.220
24.	Benzo(c)phenanthrene	--	3.64	--	--	--	6.226
25.	1,1'-Dinaphthyl	--	2.99	--	3.167	--	6.893
26.	1,2'-Dinaphthyl	--	3.29	--	--	--	6.887
27.	2,2'-Dinaphthyl	--	4.01	--	--	3.879	6.881
28.	Perylene	4.70	4.61	3.92	--	4.559	6.976
29.	Benzo(a)pyrene	4.44	4.38	4.11	--	4.425	6.970
30.	Benzo(e)pyrene	4.60	4.46	--	--	--	6.975
31.	Benzo(b)crysene	--	5.00	--	--	5.000	7.631
32.	Benzo(g,h,i)perylene	5.00	4.83	4.45	--	> 5	7.720
33.	Dibenz(a,c)anthracene	5.00	4.93	4.64	--	> 5	7.637
34.	Dibenz(a,h)anthracene	4.68	4.94	4.60	--	> 5	7.631
35.	Dibenz(a,j)anthracene	--	--	4.11	--	--	7.631
36.	Picene	--	5.03	4.63	--	> 5	7.637
37.	Anthanthrene	--	4.80	4.42	--	> 5	7.714
38.	Coronene	--	--	4.77	--	> 5	8.464
39.	Rubicene	--	--	5.36	--	> 5	9.143
40.	Dibenz(e,h)pyrene	--	--	--	--	> 5	8.387
41.	Dibenz(a,h)pyrene	--	--	--	--	> 5	8.381
42.	Dibenz(a,e)pyrene	--	--	5.37	--	--	8.053
43.	9,9'-Bianthryl	--	4.30	--	--	--	9.714
44.	9,9'-Phenanthryl	--	4.64	--	--	--	9.714

The trigonal additivity procedure considers the contribution of triatoms, or trios of non-bonded atoms which are mutually connected to a central atom. For the non-substituted PNAs, we have two different types of triatoms and the expression for a given property on the basis of trigonal additivity is

$$P = ma_{110} + (n - m) a_{111} \qquad (3)$$

where a_{110} is the contribution of the HA_1A_1-A_1 triatom and a_{111} is the contribution of the $A_1A_1A_1$-A_2 triatom.

As might be expected, the above procedures will not yield very satisfactory results since each only employs two parameters. However, Somayazulu and Zwolinski (23) pointed out that the trigonal procedure may be improved by recognizing the existence of two types of aromatic carbon atoms (23). Figure 1 shows the two types of triatom. The first type, which we designate as A_1 is an aromatic carbon atom connected to a hydrogen atom, while the second kind, A_2, is not connected to a hydrogen atom. As a consequence of the introduction of two types of carbon atoms, as shown in Figure 1, the two types of trigonal parameters are expanded to six parameters as shown in Figure 2, i.e.,

$$P = Z_1\phi_1 + Z_2\phi_2 + Z_3\phi_3 + Z_4\phi_4 + Z_5\phi_5 + Z_{23}\Delta_{23} + Z_{24}\Delta_{24} + Z_{34}\Delta_{34} \qquad (4)$$

where Z_1 is the number of type "1a" and "1b" triatoms and ϕ_1 is the contribution of such groups. The parameters Z_2, Z_3, Z_4 and Z_5 are the numbers of type 2, 3, 4 and 5 triatoms, respectively and ϕ_2, ϕ_3, ϕ_4 and ϕ_5 are the respective contributions of these groups. The coefficients Z_{23}, Z_{24} and Z_{34} are correspondingly the number of bonds between type 2 and type 3, type 2 and type 4, and type 3 and type 4 triatoms, while Δ_{23}, Δ_{24} and Δ_{34} are the respective contributions of such interactions.

Although the full eight parameter equation was employed in correlating and estimating very precisely measured properties, such as enthalpies of combustion, very satisfactory results are often achieved by only considering the contributions of the first five parameters (28), i.e.

$$P = Z_1\phi_1 + Z_2\phi_2 + Z_3\phi_3 + Z_4\phi_4 + Z_5\phi_5 \qquad (5)$$

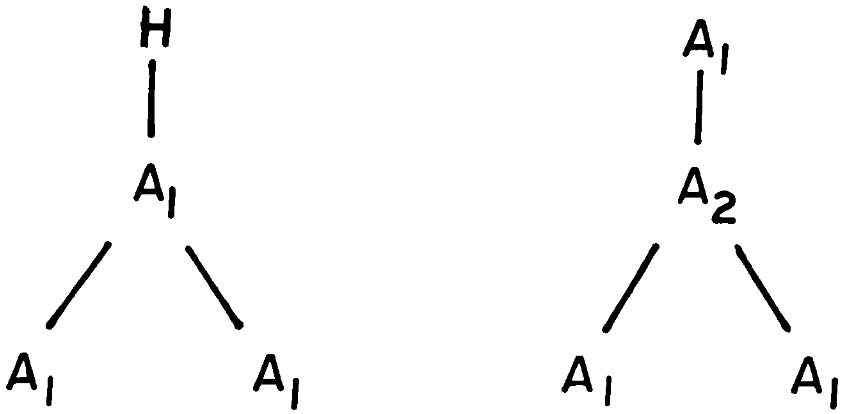
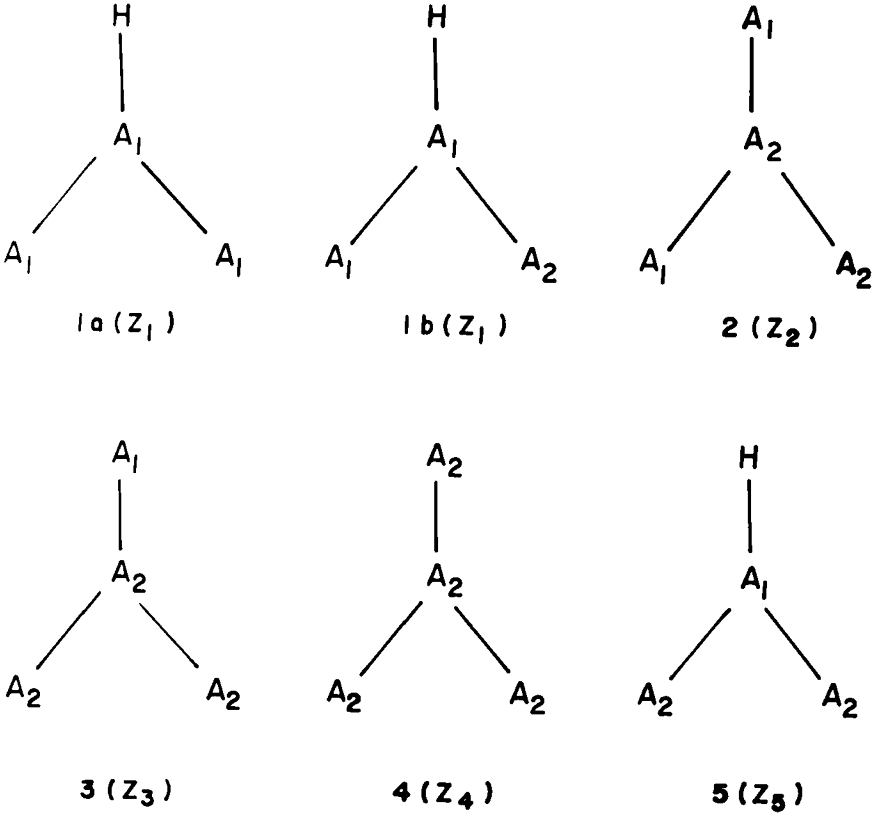


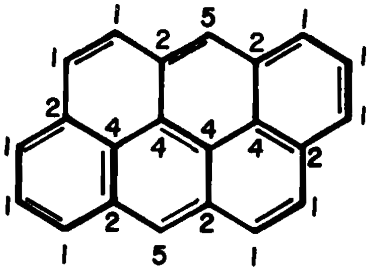
FIGURE 1



1a (Z_1) 1b (Z_1) 2 (Z_2)

3 (Z_3) 4 (Z_4) 5 (Z_5)

FIGURE 2



$Z_1 = 10$ $Z_2 = 6$ $Z_3 = 0$

$Z_4 = 4$ $Z_5 = 2$

$Z_{23} = 0$ $Z_{34} = 0$ $Z_{24} = 6$

FIGURE 3

Figure 3 illustrates how the calculation of trigonal additivity parameters is done using anthanthrene as an example.

RESULTS AND DISCUSSION

Connectivity index is a parameter indicating the size and extent of branching of a molecule. It is very simple to calculate and yet has been shown by many workers to correlate well with molecular properties such as boiling points, water solubility and partition coefficients (29,30). Its application in correlating gas chromatographic retention has also been shown (31). In RP-HPLC, connectivity has also been applied (10, 19, 32). While extensive attempts have been made to correlate physico-chemical properties of molecules with retention on RP-HPLC, such is not the case for NP-HPLC using polar bonded phase.

Table 1 is a compilation of the retention indices and connectivity values of the 44 PNAs used for this study. The chromosorb LC-9 were obtained experimentally in our laboratory. The remainder of the data were gathered from references indicated. The diamine data (21) are divided into two columns because two different mobile phases were used. This is due to the fact that the diamine stationary phase retains the higher ring PNAs very strongly and requires a more polar mobile phase to elute them within a reasonable period of time (21).

Table 2 tabulates the values of trigonal additivity parameters for the 44 PNAs. Trigonal additivity successfully correlates the properties of alkyl compounds (33) and aromatic compounds (23). While it would be interesting to test the applicability of trigonal additivity as a method of correlating retention indices of alkyl aromatic compounds, doing so is not possible at the present time. The reason is that parameters used in the alkyl and aromatic trigonal additivity procedures are quite different. Enough data on alkyl aromatic retention indices would have to be available to determine the ten or more alkyl type parameters and the six aromatic triatomic parameters plus several additional parameters relating to where the alkyl chain was attached to the aromatic molecule. Nonetheless, the data available do provide a convenient handle for the purpose of introducing a new methodology and for making direct parallel comparisons with the known Randic connectivity index.

Because of the widespread and proven utility of connectivity, we consider it will serve us well to include it in our study for comparison purposes. The results for correlation of retention data on nitrogen-containing phases with connectivity are presented in Table 3. The number of data points included in the analysis of each set of data is also give. For the diamine (6% CH_2Cl_2), only compounds whose retention values are definitely known are included in the analysis.

The correlation coefficients (r^2) using connectivity for all four stationary phases are suprisingly poor when all the available data are analyzed. Several workers (10,29-31) have applied connectivity in related fields and found good correlations with physico-chemical properties such as water solubility, hydrophobicities and partition coefficients which are considered to be important factors in chromatography. The results for the very polar diamine stationary phase where strong electronic interaction occurs are particularly noteworthy. These poor correlations seem to suggest that connectivity may not be a good descriptor for the separation of PNAs on the polar nitrogen-containing bonded

TABLE 2

Trigonal Additivity Values

Compound	Z_1	Z_2	Z_3	Z_4	Z_5	Z_{23}	Z_{24}	Z_{34}
1. Benzene	6	0	0	0	0	0	0	0
2. Biphenyl	10	2	0	0	0	0	0	0
3. Naphthylene	8	2	0	0	0	0	0	0
4. -2 phenyl	11	4	0	0	1	0	0	0
5. -1,2,3,4 Tetraphenyl	24	4	2	4	0	0	4	2
6. Acenaphthylene	8	3	0	1	0	0	3	0
7. p-Terphenyl	14	4	0	0	0	0	0	0
8. o-Terphenyl	14	2	2	0	0	2	0	0
9. m-Terphenyl	13	4	0	0	1	0	0	0
10. Anthracene	8	4	0	0	2	0	0	0
11. -9,10-diphenyl	18	2	4	2	0	0	2	4
12. Phenanthrene	10	2	2	0	0	2	0	0
13. Fluoranthene	10	1	4	1	0	0	1	2
14. -benzo(b)	11	1	6	1	1	1	0	3
15. -benzo(j)	12	2	4	2	0	1	1	5
16. -benzo(k)	10	3	4	1	2	0	1	2
17. -benzo(g,h,i)	10	3	2	3	0	0	3	2
18. Pyrene	10	4	0	2	0	0	4	0
19. Chrysene	12	2	4	0	0	2	0	0

20.	Naphthacene	8	6	0	0	4	0	0	0
21.	p-Quaterphenyl	18	6	0	0	0	0	0	0
22.	Triphenylene	12	0	6	0	0	0	0	0
23.	Benz(a)anthracene	10	4	2	0	2	2	0	0
24.	Benzo(c)phenanthrene	12	3	2	1	0	2	1	2
25.	1,1'-Dinaphthyl	14	2	4	0	0	2	0	0
26.	1,2'-Dinaphthyl	13	4	2	0	1	2	0	0
27.	2,2'-Dinaphthyl	12	6	0	0	2	0	0	0
28.	Perylene	12	2	4	2	0	0	2	4
29.	Benzo(a)pyrene	11	4	2	2	1	1	3	1
30.	Benzo(e)pyrene	12	2	4	2	0	0	2	2
31.	Benzo(b)chrysene	12	4	4	0	2	2	0	0
32.	Benzo(g,h,i)perylene	12	4	2	4	0	0	4	2
33.	Dibenz(a,c)anthracene	12	2	6	0	2	0	0	0
34.	Dibenz(a,h)anthracene	12	4	4	0	2	4	0	0
35.	Dibenz(a,j)anthracene	12	4	4	0	2	4	0	0
36.	Picene	14	2	6	0	0	2	0	0
37.	Anthanthrene	10	6	0	4	2	0	6	0
38.	Coronene	12	6	0	6	0	0	6	0
39.	Rubicene	14	0	8	4	0	0	0	8
40.	Dibenz(e,h)pyrene	13	3	4	3	1	1	2	3
41.	Dibenz(a,h)pyrene	12	4	4	2	2	2	2	2
42.	Dibenz(a,e)pyrene	13	3	4	3	0	0	3	4
43.	9,9'-Binanthryl	16	4	4	2	2	4	0	4
44.	9,9'-Phenanthryl	16	3	6	1	2	3	0	3

TABLE 3

Results of regression analysis of retention data using connectivity indices.

	LC-9 NH_2	Bondapek NH_2	Pyrrolidone	Diamine C_6H_{12}	Diamine 6% CH_2CL_2
N	19	35	26	15	11
r^2	0.879	0.714	0.741	0.575	0.258
RMSE	0.401	0.525	0.585	0.506	0.463
b	-0.200	0.299	0.044	1.038	3.143
a	0.647	0.530	0.552	0.361	0.151
N'	16	25	21	9	9
$r^{2'}$	0.988	0.989	0.953	0.912	0.979
RMSE'	0.131	0.109	0.237	0.293	0.585
b'	-0.299	-0.356	-0.017	0.074	-0.222
a'	0.690	0.690	0.600	0.640	0.678

N = number of data points

r^2 = correlation coefficient

RMSE = root mean square error

b = intercept :
: in $P = a\chi + b$
a = coefficient :

non-primed quantities = for all compounds

primed quantities = for condensed compounds only phase NP-HPLC. It had been proposed that retentions for the polar amino bonded phase are due to π-electron interaction between the PNAs and the polar functional groups in the stationary phase (1). Since connectivity is a topological parameter pertaining more to structure and size of a molecule, it may be inadequate to account of the kind of electronic intereactions proposed. However, Markowski (34) did report good correlation between connectivity and liquid chromatographich retention of PNA on alumina where adsorption does occur.

Since the results for the diamine data using first order connectivity index are so strikingly poor, a closer examination is warranted. We found that for some compounds, the log I values and their corresponding connectivity indices are obvious "outliers". For instance, 1,2,3,4-tetraphenyl naphthalene (#4) has a log I value of 4.402, while its connectivity index is a large 11.720, in fact the largest of all connectivity values. Moreover, it is included only in the diamine (CH_2Cl_2) data and not present in the other data sets. Other examples are 1,1'-Dinaphthyl (#24) for the diamine (C_6H_{12}) data set and 2,2'-Dinaphthyl (#27) for the diamine (CH_2Cl_2) data. These appear to be all polyphenyl arenes. Because this is such a small set of data to affirm a definite trend, the μBondapak amine data set is examined for a similar trend. Figure 4 is a plot of the predicted retention indices of the 35 compounds against the experimental retention indices on the μBondapak amine column. As one can clearly see, the regression line slope is far from the ideal line (of 45° slope). Also with careful observation, the polyphenyl arenes are indeed the "outliers". Incidentally, the slope of the line joining only these polyphenyl arenes is quite parallel to the ideal line.

We reanalyzed the data with only the condensed compounds included. These results are given in the second half of Table 3. The correlations between connectivity and retention indices for all bonded phases improve greatly with the corresponding errors much less. The plot of predicted log I against observed log I as shown in Figure 5 is very much better, with almost all the points close to the regression line which is also almost identical in slope to the ideal line.

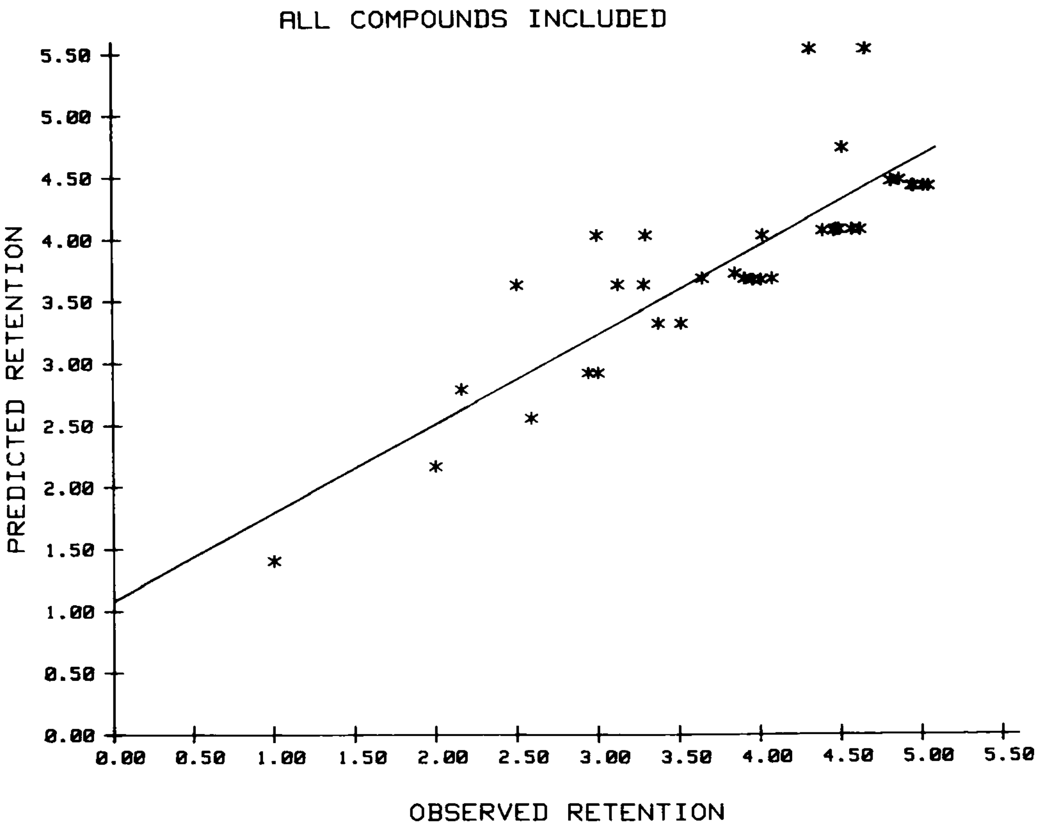

ALL COMPOUNDS INCLUDED
PREDICTED RETENTION
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
OBSERVED RETENTION

FIGURE 4

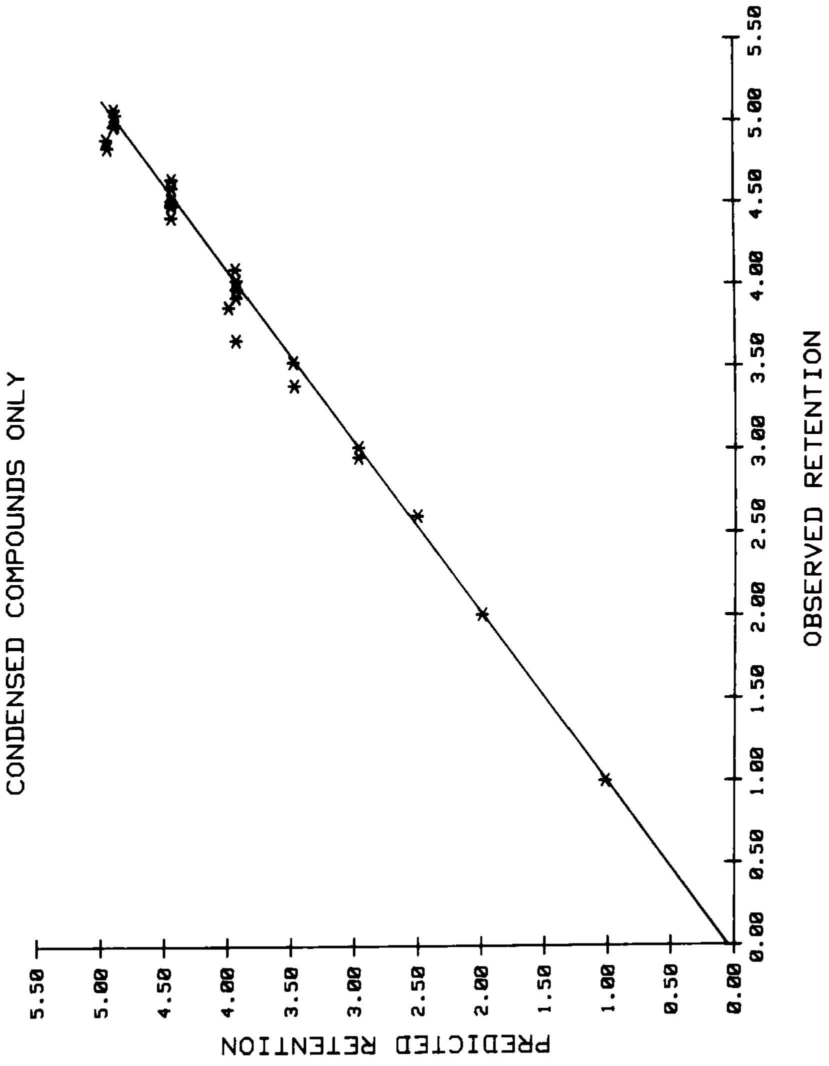

CONDENSED COMPOUNDS ONLY
PREDICTED RETENTION
OBSERVED RETENTION
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50

FIGURE 5

Table 4 summarized the correlation coefficients and the corresponding errors for using the five-parameter (Equation 5) and eight-parameter (Equation 4) equations. Contrary to the results for connectivity, the correlation for all four stationary phases, even with all the available data included in the analysis, are all much better than connectivity. The diamine (CH_2Cl_2) fared just as well. The eight-parameter equation seems to improve the results only slightly, indicating that the contribution of the last 3 terms is not significant. Therefore, we will from now base our discussions on the results of the five-parameter equation. Though not included here, the plot of predicted vs. experimental retention for the μBondapak amine data does not have the wide scatter as in the case of connectivity (Figure 4), and that the slope of the regression line is much closer to ideal. However, wherever the greatest deviation from ideal occurs, it is one of the polyphenyl arenes.

When the data are reanalyzed with only the condensed PNAs included, the results for trigonal additivity also improved, just as in the case of connectivity index. However, the change in the correlation found is not as dramatic as in the case for connectivity, especially for the diamine and μBondapak amine data where relatively more of the polyphenyl arenes is included. This difference in the change indicates that the trigonal additivity is a more stable and better descriptor than connectivity for the kind of interaction that is predominant in these polar bonded phases.

These results also indicate that the polyphenyl arenes behave differently from the other PNAs in the same ring class on these polar bonded phases NP-HPLC. The reduction in the errors for μBondapak and the diamine data were substantial when the polyphenyl arenes are not included in the analysis. Similar observation of deviation of non-planar PNAs was also reported in gas chromatography (34) and work of Hammers and co-workers (12).

It is a general consensus among many workers that nitrogen-containing polar bonded phase used in NP-HPLC separate PNAs by ring sizes (1,11,12,20,21) and that the principal interaction responsible for retention is that between the π electrons of the PNAs and the nonbonded electrons on the nitrogen functional group. Thus, although connectivity index has been shown to be a good predictor

TABLE 4

Results of regression analysis of retention data using trigonal additivity.

	LC-9 NH_2	Bondapek NH_2	Pyrrolidone	Diamine C_6H_{12}	Diamine 6% CH_2CL_2
N	19	35	26	15	11
$r^2(5)$	0.989	0.912	0.948	0.916	0.952
RMSE	0.136	0.313	0.238	0.269	0.158
$r^2(8)$	0.991	0.938	0.959	0.935	0.979
RMSE	0.144	0.278	0.275	0.292	0.165
N'	16	25	20	9	9
$r^2(5)'$	0.992	0.994	0.959	0.972	0.998
RMSE′	0.125	0.0087	0.250	0.252	0.0040
$r^2(8)'$	0.995	0.995	0.968	*	*
RMSE	0.117	0.0091	0.250		

N = number of data points

r^2 = correlation coefficient

RMSE = root mean square error

non-primed quantities = for all compounds

primed quantities = for condensed compounds only

* = insufficient data for meaningful results

for a number of processes and interactions especially where structure and size of the molecules directly or indirectly play a major role, it does not do as well with polar bonded phase NP-HPLC data because the major interaction responsible is not strongly structure related. As one can see, connectivity indicates high retention values for these polyphenyl arenes. An obvious example is the connectivity value of 11.72 for 1,2,3,4-tetraphenyl naphthalene.

Trigonal additivity on the other hand was developed and evolved by Zwolinski from Brown's model for the quantum mechanical calculation of the electronic energies of organic molecules and should then be a good predictor for properties involving electronic interactions such as the one we have with the nitrogen-containing polar bonded phases. Our results affirm this expectation. The case with polyphenyl arenes is that electronic intereaction between them and the amino group on these phases must have been adversely affected despite the fact that the number of aromatic structures is greater. It is known that they are not as rigid and planar. This can therefore reduce the conjugation of the system and thus weaken the electronic interactions to less than what their structures would predict. Because trigonal additivity combines 6 parameters which must have adequately represented the contribution of the electronic factors and not inordinately biased by molecular structure, trigonal additivity does better in correlating retention in the polar bonded phase NP-HPLC as our results show.

We have shown that trigonal additivity provides good correlation with retention in the polar bonded phase NP-HPLC. From such results we may infer the relative importance of the types of interactions possible, in this case the electronic interactions between the PNAs and the amino group. We have shown also how useful correlation studies can be in indicating anomalies as in the case of polyphenyl arenes. However, to be able to really predict retention indices accurately, more data need to be available for more indepth analysis. Nonetheless, trigonal additivity, considering how well it has done with respect to connectivity, should find wider applications and we hope our introduction will pave the way for others and stimulate discussion.

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