Prediction of Gas Chromatographic Retention Indexes of Mono-, Di- and Trimethylbiphenyls

B. Bogdanov

Department of Chemistry, University of Skopje, Macedonia, Yugoslavia

Two graph-theoretical models have been developed to describe the relationship between the molecular structure of methyl-, dimethyl- and trimethylbiphenyls and their gas chromatographic retention characteristics. The retention time of these compounds was predicted as a linear relationship between the retention time and first-order mean square distance index. A multiple linear equation, containing five terms, was also developed. The sixth-order path/cluster connectivity index representing substitution patterns of mono-, di- and trimethylbiphenyls is discussed. In addition, the use of mean square indices in a quantitative structure-retention relationship study was tested for the first time.

INTRODUCTION

Quantitative Structure-Retention Relationship (QSRR) investigations[1] have developed rapidly in the past few years, as evidenced by the number of papers published.[2–17]

Retention in gas chromatography is the result of competitive solubility of the solute between mobile and stationary phases. The partition of solute between these two phases is determined by the molecular structure and chemical properties of the solute. These differences govern the retention behavior through the column.[18] Quantitative description of molecular structure enables to generate a model relating molecular structure to chromatographic retention times. In the present study, we investigated the predictability of the gas chromatographic retention time of mono-, di- and trimethylbiphenyls using topological indices. This approach of chromatographic retention time is applied because of the conformational flexibility of the majority of the methyl-substituted biphenyls, which makes three dimensional modeling of the chemical structure not feasible.

Methyl-substituted biphenyls were selected for this investigation because they occur in the aromatic fraction of crude oils and sediment of coal extract.[19,20] Identification of some isomers of methyl- substituted biphenyls in crude oils by gas chromatography has been reported[19].

In addition, depletion in the abundance of 2-methylbiphenyl, relative to that of 3-methylbiphenyl, with increasing depth and maturity in the sediment column, has also been reported.[20]

In this publication, we report linear and multiple linear models for predicting linear-temperature programmed gas chromatographic retention times of mono-, di- and trimethylbiphenyls by using graph-theoretical indices based on topological distances and connectivity. Forty graph theoretical indices were tested. The best one-variable equation was obtained with the first-order mean square distance index. A final pool of five indices, as independent variables in the multiple linear regression, were obtained. The five graph-theoretical indices used in this study are listed in Table I. Linear and multiple correlation coefficients between the calculated and experimental values are 0.868 and 0.965, respectively. A sixth-order path/cluster connectivity index was used in the multiple regression equation as a descriptor representing the substitution pattern of mono-, di- and trimethylsubstituted biphenyls. In addition, the use of mean square distance indices in a QSRR study was tested for the first time.

TABLE I

Symbols for graph-theoretical indices used in the regression analyses

Symbol	Type of index
$D4$	Fourth-order mean square distance index
$M2$	Zagreb group index
$^6\chi_{pc}$	Sixth-order path/cluster connectivity index
$^7\chi_{ch}$	Seventh-order connectivity index
$^4\chi^v$	Fourth-order valence connectivity index

METHOD OF CALCULATIONS

Forty graph-theoretical indices were calculated for each nono-, di- and trimethylbiphenyl. The indices calculated include: the Zagreb group indices,[21] Platt's number,[22] Gordon-Scantlebury's index,[23] Wiener's number,[24] polarity number,[24] Balaban's index,[25] Altenburg's polynomial,[26] mean square distance indices,[27] and nonvalent and valent molecular connectivity indices.[28,29] A subclass of the nonvalent and valent molecular connectivity path, cluster and/or path/cluster type indices were also calculated.[28,29] In a single variable model, only the first-order mean square distance index is useful for predicting the experimental retention time of mono-, di- and trimethylbiphenyls. Multiple linear regression performed on the forty indices resulted in a five-descriptor equation. The indices used in the multiple regression are displayed in Table I. Several extensive reviews have been published[28-30] and give a detailed description of the theory and method of calculating the indices used in the present investigation. In presenting equations for the indices shown in Table I, we will use the graph-theoretical language of references.[28-30]

(i) The general equation for calculating the mean square distance topological indices of the s-th order is,[27]

$$D^{(s)} = \left[\frac{\displaystyle\sum_{i=1}^{N} \sum_{k=1}^{k_{max}} (A_k^2)_{ii} \cdot k^s}{\displaystyle\sum_{i=1}^{N} \sum_{k=1}^{k_{max}} (A_k^2)_{ii}} \right]^{1/s} \tag{1}$$

where; $s = 1, 2, 3$ or 4; $(A_k^2)_{ii}$ is the square of the higher order adjacency matrices; k is the number of neighbors of vertex i.

(ii) The Zagreb group index, $M2$, may be calculated by means of the following formula[21-30]

$$M2 = \sum_{\text{all edges}} A_i \cdot A_j = \sum_{\text{all edges}} (A_i^2)_{ii} \cdot (A_i^2)_{jj} \tag{2}$$

(iii) The nonvalent ($^n\chi_t$) and valent molecular connectivities ($^n\chi_t^v$)   are calculated by considering various fragments of the molecule:[28,31]

$$^n\chi_t = \sum_{s=1}^{n_m} \left(\prod_i^{m=1} \delta_1 \right)_s^{-1/2} \tag{3}$$

$$^n\chi_t^v = \sum_{s=1}^{n_m} \left(\prod_i^{m=1} \delta_1^v \right)_s^{-1/2} \tag{4}$$

where; $^n\chi_t$ is the n-th order term of type t (t = path, cluster, path/cluster, or chain) n_m is the number of connected subgraphs of type t, m is the number of edges, and δ and δ^v are the vertex nonvalence and valence values, respectively. The nonvalence value, δ, is equal to the number of nonhydrogen atoms connected to the atom of interest and is assigned to each atom in a molecule excluding the hydrogen atoms. The valence delta value, δ^v, is calculated from the following equation,

$$\delta^v = \frac{Z^v - h}{Z - Z^v - 1} \tag{5}$$

Where Z^v is the number of valence electrons in the atom, h is the number of hydrogen atoms bound to that atom, and Z is its atomic number.

All topological indices were calculated according to the formulae in references[28,30] using a computer program written in FORTRAN 77.

The experimental data used in this investigation are taken from the unpublished work[32] of Laboratory of Petroleum Geochemistry Group, School of Applied Chemistry, Curtin University of Technology, Perth, W. Australia.

RESULTS AND DISCUSSION

The experimental retention times and the topological indices of biphenyl and of the mono-, di- and trimethyl derivatives examined in the present study are shown in Table II.

TABLE II
EXPERIMENTAL RETENTION TIMES AND GRAPH-THEORETICAL INDICES* OF
BIPHENYL, MONO-, DI- AND TRIMETHYLBIPHENYLS

Compound	RT**	D1	D4	M2	$^6\chi_{PC}$	$^7\chi_{CH}$	$^4\chi^V$
Biphenyl	40.50	3.00	3.98	65	2.121	0.118	1.261
2-Methylbiphenyl	–	3.08	4.01	73	3.398	0.190	1.515
3-Methylbiphenyl	46.50	3.15	4.17	72	2.848	0.190	1.455
4-Methylbiphenyl	47.00	3.23	4.40	72	2.619	0.190	1.377
2,3-Dimethylbiphenyl	49.97	3.20	4.16	81	4.526	0.234	1.682
2,4-Dimethylbiphenyl	48.58	3.27	4.36	80	4.080	0.234	1.755
2,5-Dimethylbiphenyl	48.22	3.22	4.18	80	4.397	0.234	1.665
2,6-Dimethylbiphenyl	44.47	3.14	4.03	81	4.946	0.234	1.875
3,4-Dimethylbiphenyl	55.95	3.33	4.46	80	3.634	0.234	1.552
3,5-Dimethylbiphenyl	53.42	3.27	4.29	79	3.724	0.234	1.772
2,2'-Dimethylbiphenyl	43.25	3.15	4.04	81	4.796	0.263	1.750
2,3'-Dimethylbiphenyl	47.78	3.23	4.20	80	4.064	0.263	1.709
2,4'-Dimethylbiphenyl	48.58	3.31	4.43	80	3.904	0.263	1.630
3,3'-Dimethylbiphenyl	53.67	3.31	4.36	79	3.578	0.263	1.649
3,4'-Dimethylbiphenyl	54.28	3.38	4.58	79	3.345	0.263	1.571
4,4'-Dimethylbiphenyl	54.78	3.46	4.80	79	3.116	0.263	1.492
2,3,4-Trimethylbiphenyl	58.33	3.35	4.42	89	5.584	0.258	1.887
2,3,5-Trimethylbiphenyl	55.67	3.31	4.27	88	5.700	0.258	1.957
2,3,6-Trimethylbiphenyl	52.53	3.26	4.17	89	6.322	0.258	2.000
2,4,5-Trimethylbiphenyl	50.83	3.31	4.33	88	5.743	0.258	2.240
2,4,6-Trimethylbiphenyl	62.88	3.41	4.51	88	4.942	0.258	1.833
3,4,5-Trimethylbiphenyl	56.50	3.37	4.43	88	5.394	0.258	1.899
2,3,2'-Trimethylbiphenyl	51.01	3.28	4.20	89	5.855	0.307	1.918
2,3,3'-Trimethylbiphenyl	55.47	3.35	4.36	88	5.197	0.307	1.876
2,3,4'-Trimethylbiphenyl	56.50	3.43	4.58	88	5.031	0.307	1.797
2,4,2'-Trimethylbiphenyl	49.67	3.35	4.41	88	5.487	0.307	1.991
2,4,3'-Trimethylbiphenyl	54.37	3.43	4.56	87	4.745	0.307	1.950
2,4,4'-Trimethylbiphenyl	55.01	3.50	4.77	87	4.585	0.307	1.871
2,5,2'-Trimethylbiphenyl	49.01	3.30	4.22	88	5.739	0.307	1.901
2,5,3'-Trimethylbiphenyl	53.88	3.37	4.37	87	5.066	0.307	1.859
2,5,4'-Trimethylbiphenyl	54.83	3.45	4.59	87	4.902	0.307	1.780
2,6,2'-Trimethylbiphenyl	46.01	3.22	4.07	89	6.446	0.307	2.093
2,6,3'-Trimethylbiphenyl	49.78	3.30	4.23	88	5.555	0.307	2.070
2,6,4'-Trimethylbiphenyl	50.83	3.37	4.45	88	5.458	0.307	1.990
3,4,2'-Trimethylbiphenyl	56.00	3.41	4.51	88	4.860	0.307	1.806
3,4,3'-Trimethylbiphenyl	61.71	3.49	4.66	87	4.364	0.307	1.746
3,4,4'-Trimethylbiphenyl	62.01	3.56	4.88	87	4.132	0.307	2.667
3,5,2'-Trimethylbiphenyl	53.28	3.35	4.33	87	4.878	0.307	2.027
3,5,3'-Trimethylbiphenyl	59.50	3.43	4.48	86	4.458	0.307	1.966
3,5,4'-Trimethylbiphenyl	60.02	3.50	4.71	86	4.221	0.307	1.887

*Abbreviation used are shown in Table I.   **Exp.retention time [32].

It is apparent that the retention time of substituted biphenyls is predominantly influenced by the position of the methyl substituents, while the influence of the number of methyl groups is secondary. The first compounds to be eluted are those having a methyl group at position 2, followed by 3-substituted and finally 4-substituted derivatives.[19,32,35] For the dimethylbiphenyl series in which one substituent is in the *ortho*-position, 2,3-dimethylbiphenyl is the one with the longest elution time. Of the *meta*- and *para*-substituted derivatives, 3,4-dimethylbiphenyl is eluted last.

From Table II we see that the first-order mean square index is a good descriptor for predicting the linear temperature programmed gas chromatographic retention time of mono-, di- and trimethyl biphenyls. However, the number of biphenyl pseudo homologous derivatives eluted before biphenyl itself increases with increasing phase selectivity.[35] On Apiezon L stationary phase 2-methylbiphenyl elutes before biphenyl, and furthermore on SP1000 stationary phase 2,3'-dimethylbiphenyl elutes before biphenyl.[35]
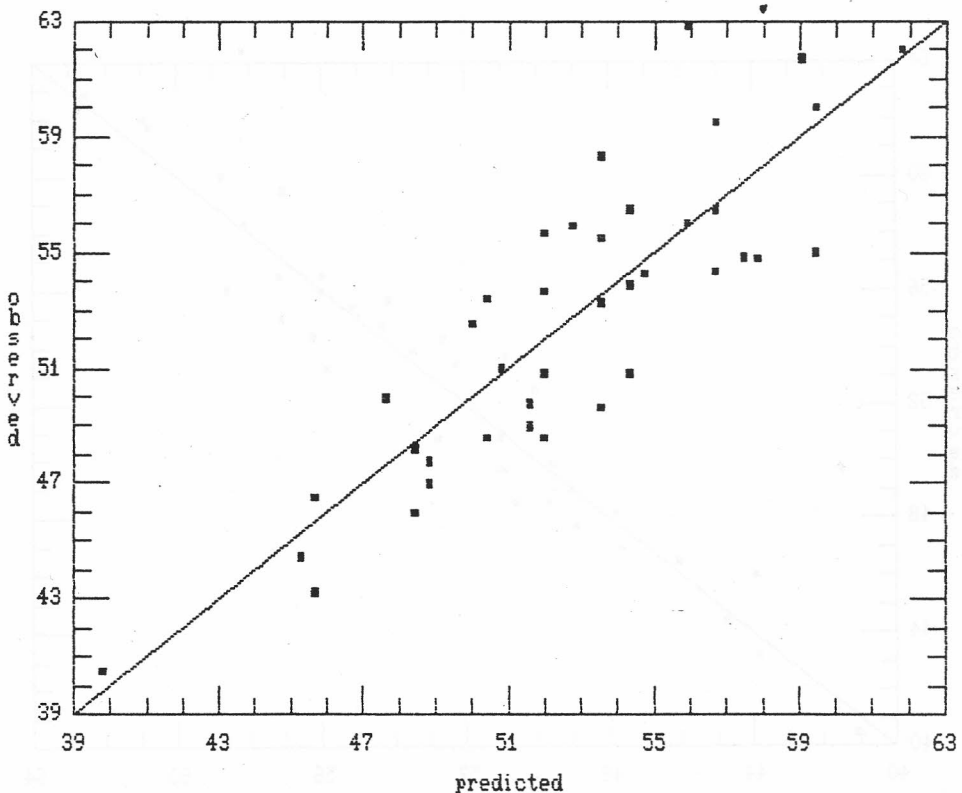

Figure 1. Plot of observed retention times versus predicted values using eg. 6.

Forty graph-theoretical indices were tested and the best single descriptor equation for predicting the retention time of the mentioned molecules employs the first-order mean square distance index ($D1$),

$$RT = a + b \cdot D1 \tag{6}$$

$$a = -78.12; \ b = 39.30; \ N = 40; \ r = 0.868; \ s = 2.63; \ F^{1.37} = 113$$

This equation was used to calculate the retention time of the mono-, di and trimethylbiphenyls and the values obtained are given in Table III. Figure 1 shows a cross-plot between the predicted and the experimental retention times. Agreement between the predicted and observed retention times suggests that the gas chromatographic behavior of mono-, di- and trimethyl biphenyls may depend critically on the shape of the molecular network. In earlier studies on the mean square distance indices [33,34] it was found that for cyclic graphs $D^{(s)}$ (eq. 1) has a relatively high degeneracy with increasing branching.
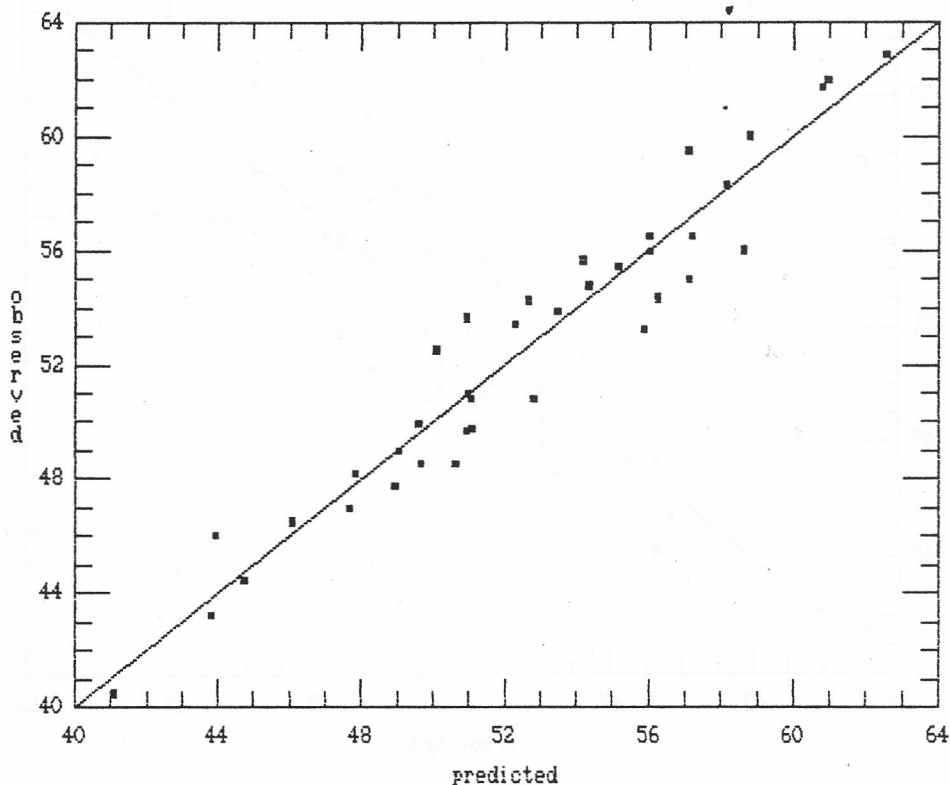

Figure 2. Plot of observed retention times versus predicted values using eq. 7.

TABLE III
EXPERIMENTAL AND THEORETICAL RETENTION TIMES OF BIPHENYL, MONO-,
DI- AND TRIMETHYLBIPHENYLS

Compound	Retention times (min.)		
	Experimental*	Theoretical	
		eqn. 6	eqn. 7
Biphenyl	40.50	39.783	41.087
2-Methylbiphenyl	-	42.926	43.260
3-Methylbiphenyl	46.50	45.677	46.077
4-Methylbiphenyl	47.00	48.821	47.687
2,3-Dimethylbiphenyl	49.97	47.642	49.599
2,4-Dimethylbiphenyl	48.58	50.393	50.624
2,5-Dimethylbiphenyl	48.22	48.428	47.838
2,6-Dimethylbiphenyl	44.47	45.284	44.735
3,4-Dimethylbiphenyl	55.95	52.751	56.026
3,5-Dimethylbiphenyl	53.42	50.393	52.282
2,2'-Dimethylbiphenyl	43.25	45.677	43.810
2,3'-Dimethylbiphenyl	47.78	48.821	48.928
2,4'-Dimethylbiphenyl	48.58	51.965	49.656
3,3'-Dimethylbiphenyl	53.67	51.965	50.926
3,4'-Dimethylbiphenyl	54.28	54.716	52.650
4,4'-Dimethylbiphenyl	54.78	57.860	54.324
2,3,4-Trimethylbiphenyl	58.33	53.537	58.138
2,3,5-Trimethylbiphenyl	55.67	51.965	54.172
2,3,6-Trimethylbiphenyl	52.53	50.000	50.082
2,4,5-Trimethylbiphenyl	50.83	51.965	52.798
2,4,6-Trimethylbiphenyl	62.88	55.895	62.563
3,4,5-Trimethylbiphenyl	56.50	54.323	57.191
2,3,2'-Trimethylbiphenyl	51.01	50.786	50.968
2,3,3'-Trimethylbiphenyl	55.47	53.537	55.140
2,3,4'-Trimethylbiphenyl	56.50	56.681	56.008
2,4,2'-Trimethylbiphenyl	49.67	53.537	50.932
2,4,3'-Trimethylbiphenyl	54.37	56.681	56.241
2,4,4'-Trimethylbiphenyl	55.01	59.432	57.095
2,5,2'-Trimethylbiphenyl	49.01	51.572	49.041
2,5,3'-Trimethylbiphenyl	53.88	54.323	53.468
2,5,4'-Trimethylbiphenyl	54.83	57.467	54.310
2,6,2'-Trimethylbiphenyl	46.01	48.428	43.943
2,6,3'-Trimethylbiphenyl	49.78	51.572	51.068
2,6,4'-Trimethylbiphenyl	50.83	54.323	51.054
3,4,2'-Trimethylbiphenyl	56.00	55.895	58.623
3,4,3'-Trimethylbiphenyl	61.71	59.039	60.812
3,4,4'-Trimethylbiphenyl	62.01	61.790	60.949
3,5,2'-Trimethylbiphenyl	53.28	53.537	55.861
3,5,3'-Trimethylbiphenyl	59.50	56.681	57.079
3,5,4'-Trimethylbiphenyl	60.02	59.432	58.793

* Experimental data are from ref.   [32]

Subsequently, a multivariate model that better differentiated isomeric mono-, di- and trimethylbiphenyls was developed. A total of 40 graph-theoretical indices were tested. The stepwise variable selection procedure[36] was used. When a high collinearity is detected ($R > 0.90$), one or more of the offending topological indices is removed from consideration. A final pool of five indices, as independent variables in the multiple linear regression, were obtained. The multivariate regression of retention times with five descriptors is presented in Table IV, eq. 7. An examination of the residuals (Figure 3) shows a fairly random patern. The correlation matrix for
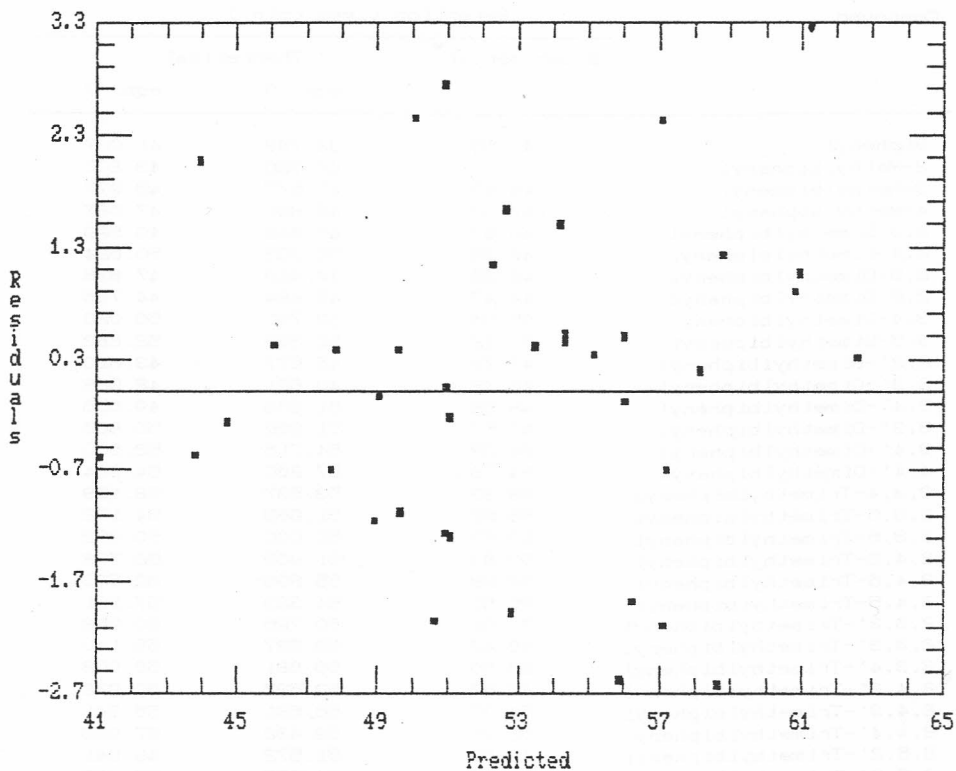
Figure 3. Plot of residuals versus calculated retention times using eq. 7.

the five indices used in eq. 7 shows no high correlation between the parameters (Table V). The retention times predicted by this equation are shown in Table III and Figure 2. A plot of the experimental vs. predicted retention times yielded

$$RT_{exp.} = a + b \cdot RT_{pred.}$$
$$a = 6 \cdot 10^{-12}; \; b = 1; \; r = 0.965; \; s = 1.39; \; F^{1,37} = 499$$

It is evident from Table III that the elution order of 33 out of 40 mono-, di- and trimethylbiphenyls is correct; however, experimental retention times for six compounds (three pairs) are the same.[19,32] Moreover, variation of the retention times with temperature is influenced primarily by the position of methyl substituent, the influence of the number of substituents being secondary. For sterically hindered biphenyls substituted at positions 2- and 6- the temperature increment is lower.

TABLE IV

Multiple regression coefficients and statisctical data for model 2

	Equation 7	
	Coefficient	
constant	−108.00 (± 8.58)	$S = 1.48$
D4	−6.28 (± 3.05)	$F^{5,33} = 89$
M2	3.31 (± 0.30)	$R^2 = 0.921$
$^6\chi_{pc}$	−12.80 (± 1.42)	$N = 40$
$^7\chi_{ch}$	−102.72 (±13.09)	
$^4\chi^v$	−1.58 (± 1.53)	

TABLE V

Correlation coefficient relationship of topological indices used in eq. 7

	D4	M2	$^6\chi_{pc}$	$7\chi_{ch}$	$4\chi^v$
D4	1.000				
M2	0.350	1.000			
$^6\chi_{pc}$	−0.099	0.882	1.000		
$^7\chi_{ch}$	0.508	0.870	0.644	1.000	
$4\chi^v$	0.249	0.778	0.701	0.668	1.000

In order to predict the gas chromatographic retention characherics of substituted biphenyls, many authors have described attempts to assign descriptors that represent their substitution pattern.[4,5,14,35] Robbat *et. al.*[5] derived position descriptors, as independent variables, to account for substituent interaction in chlorinated biphenyls. For example, indicator TWO represents the number of chlorine atoms present at the 2,2',6 and 6' positions. Positions 6 and 6' are considered equivalent to position 2 and 2', respectively. Since there are four such possible positions, indicator TWO can have values from 0 to 4. In the same way indicator THREE accounts for the number of chlorine atoms present at the 3,3' and 5,5' positions in each ring and indicator FOUR those at 4 and 4'. Again, positions 5 and 5' are considered equivalent to position 3 and 3' and indicator THREE can have values from 0 to 4. Indicator FOUR can have values from 0 to 2 (Ref. 5.).

Hasan and Jurs[4] predicted the gas chromatographic retention time of polychlorinated biphenyls using descriptor variables representing the degree of chlorination (number of chlorine atoms), number of chlorine atoms squared, number of chlorine atoms in an *ortho* position, number of chlorine atoms in a *meta* position and *etc.*

Kriz *et al.*[35] plotted the linear dependence of retention times on the number of methyl substituents for *meta-* and *para*-substituted biphenyls, which can be ex-

pressed in a general equation. The equation can be used to estimate the retention indices of multi-substituted biphenyls having different substutuents.

In the present study, a sixth-order path/cluster connectivity index ($^6\chi_{pc}$) descriptor is used to represent the substitution pattern of mono-, di- and trimethylbiphenyls. From the data in Table II, we see that $^6\chi_{pc}$ index (as position descriptor) is the most discriminative graph-theoretical index. For *ortho-*, *meta-* and *para*-methyl-biphenyl $^6\chi_{pc}$ are 3.398, 2.848 and 2.619, respectively. In the dimethylbiphenyl series in which one substituent is in the *ortho*-position, the largest $^6\chi_{pc}$ value is that of 2.6-dimethylbiphenyl and the smallest that of the 2,4'-isomer. Also it is apparent that $^6\chi_{pc}$ values for methyl groups located at the 3-, 5- or 3'-positions are not the same. 4,4'-Dimethylbiphenyl has the smallest value of the dimethylbiphenyls. In the trimethylbiphenyl series the largest $^6\chi_{pc}$ value (6.446) is that for 2,6,2'-isomer and the smallest value (4.132) for 3,4,4'-isomer. More importantly, the $^6\chi_{pc}$ index has a different value for each of all the possible substitution patterns of an individual ring. On the other hand, the correlation coefficient between $^6\chi_{pc}$ and the retention time of mono-, di- and trimethylbiphenyls is 0.147. However, in the multiple linear regression, the model degrades significantly if this term is omitted.

CONCLUSION

We have shown that the retention time of mono-, di- and trimethylbiphenyls can be predicted by using topological indices derived from molecular structure. The mean square distance indices included in the equations were tested for the first time. It should be noted, however, that equations were developed using retention data measured on a single stationary phase. This appears to significantly limit the usefulness of the models. However, we feel that these equations can be applied to columns of similar polarity with only slight modification of the values of the coefficients. With availability of retention data on other stationary phases, it would be possible to assess the effects of the stationary phase polarity, column size, *etc.* on the coefficients in predictive equations.

However, the topological approach also has its limitations. At present, it cannot account for three-dimensional problems such as for example, isomerism around the phenyl-phenyl single bond in 2,2'-dimethylbiphenyls. However, the experimental retention times were obtained with non-polar stationary phases at 200 °C and the energy supplied at this temperature is probably greater than the energy barrier for rotation around the phenyl-phenyl bond in the structures investigated. As a result, topological factors appear to be dominant.

The sixth-order path/cluster connectivity index, as a descriptor representing substitution patterns of mono-, di- and trimethylbiphenyls, has proven to be useful and evidence suggests that it may also be applied to structurally similar compounds.

REFERENCES

1. R. K a l i s z a n , *Quantitative Structure-Chromatographic Retention Relationship,* Willey, New York, 1987.

2. W. K r a w c z y k, and G. T. P i t r o w s k i, *J. Chromatogr.* **463** (1989) 297.

3. N. D i m o v, and R. M i l i n a, *J. Chromatogr.* **463** (1989) 159.

4. M. N. H a s a n, and P. C. J u r s, *Anal. Chem.* **60** (1988) 978.

5. A. R o b b a t, Jr, G. X y r a f a s, and D. M a r s h a l l, *Anal. Chem.* **60** (1988) 982.

6. R. H. R o h r b a u g h, and P. C. J u r s, *Anal. Chem.* **60** (1988) 2249.

7. P. Y. S h r o t r i, A. M o k a s h i, and D. M u k e s h, *J. Chromatogr.* **387** (1987) 399.

8. S. M i h a r a, and H. M a s u d a, *J. Chromatogr.* **402** (1987) 309.

9. R. H. R o h r b a u g h, and P. C. J u r s, *Anal. Chem.* **59** (1987) 1048.

10. A. R o b b a t, Jr., N. P. C o r s o, P. J. D o h e r t y, and D. M a r s h a l l, *Anal. Chem.* **58** (1986) 2972.

11. A. R o b b a t, Jr., N. P. C o r s o, P. J. D o h e r t y, and D. M a r s h a l l, *Anal. Chem.* **58** (1986) 2978.

12. Z. S u p r y n o w i c z, W. M. B u d a, M. M a r d a r o w i c z, and A. P a t r y k i e j e w, *J. Chromatogr.* **333** (1985) 11.

13. L. B u y d e n s, D. L. M a s a r t, and P. G e e t l i n g s, *J. Chromatogr. Sci.* **23** (1985) 304.

14. M. D. H a l e, F. D. H i l e m a n, T. M a z e r, T. L. S h e l l, R. W. N o b l e, and J. J. B r o o k s, *Anal. Chem.* **57** (1985) 640.

15. M. K u c h a r, H. T o m k o v a, V. R e j h o l e c, and O. S k a l i c k a, *J. Chromatogr.* **333** (1985) 21.

16. R. H. R o h r b a u g h, and P. C. J u r s, *Anal. Chem.* **67** (1985) 2770.

17. A. S a b l j i ć, *J. Chromatogr.* **319** (1985) 1.

18. B. L. K a r g e r, L. R. S n y d e r, and C. E o n, *J. Chromatogr.* **115** (1975) 139.

19. K. M. C u m b e r s, R. A l e x a n d e r, and R. I. K a g i, *J. Chromatogr.* **361** (1986) 385.

20. K. M. C u m b e r s, R. A l e x a n d e r, and R. I. K a g i, *Geochim. Cosmochim. Acta* **51** (1987) 3105.

21. I. G u t m a n, and N. T r i n a j s t i ć, *Chem. Phys. Lett.* **17** (1972) 535.

22. J. R. P l a t t, *J. Chem. Phys.* **15** (1947) 419; *J. Phys. Chem.* **56** (1952) 328.

23. M. G o r d o n, and G. C. S c a n t l e b u r g, *Trans. Faraday Soc.* **60** (1964) 604.

24. H. W i e n e r, *J. Am. Chem. Soc.* **69** (1947) 17; *ibid* **69** (1947) 2636; *J. Chem. Phys.* **15** (1947) 766; *J. Phys. Chem.* **52** (1948) 425; *ibid* **52** (1948) 1082.

25. A. T. B a l a b a n, *Chem. Phys. Lett.* **89** (1982) 399.

26. K. A l t e n b u r g, *Koloid Z.* **178** (1961) 112.

27. A. T. B a l a b a n, I. M o t o p c, D. B o n c e v, and O. M e k e n y a n, *Topics Curr. Chem.* **114** (1983) 21.

28. L. B. K i e r, and L. K. H a l l, *Molecular Connectivity and Drug Research,* Academic Press, New York, 1976.

29. N. T r i n a j s t i ć, *Chemical Graph. Theory,* CRC Press, Boca Raton, FL, 1983.

30. M. B a r y s z, D. P l a v š i ć, and N. T r i n a j s t i ć, *Math. Chem.* **19** (1986) 89.

31. M. R a n d i ć, *J. Am. Chem. Soc.* **97** (1975) 6604.

32. R. A l e x a n d e r, in preparation

33. I. G u t m a n, B. R u š č i ć, N. T r i n a j s t i ć, and C. F. W i l c o x, J r., *J. Chem. Phys.* **62** (1975) 3339.

34. A. T. B a l a b a n, *Chem. Phys. Lett.* **89b** (1982) 399.

35. J. K r i z, M. P o p l, and J. M o s t e c k y, *J. Chromatogr.* **97** (1974) 3.

36. N. D r a p e r, H. S m i t h, *Applied Regression Analysis,* 2nd ed., Whiley-Interscience, New York, 1981, p. 307.

SAŽETAK

Predviđanje plinsko-kromatografskih indeksa zadržavanja mono-, di- i trimetilbifenila

B. Bogdanov

Izvedena su dva modela za predviđanje plinsko-kromatografskih indeksa zadržavanja za mono-, di- i trimetilbifenile. Modeli se temelje na topologijskim indeksima. Razmatrano je 40 topologijskih indeksa koji se obično upotrebljavaju u studiranju odnosa strukture i svojstva molekula. Dobro slaganje je postignuto sa topologijskim indeksom kvadrata srednje udaljenosti prvog reda. Takođe, izvedena je i višestruka linearna zavisnost topologijskih indeksa i indeksa zadržavanja metilbifenila.