Comparison between the Vertex- and Edge-Connectivity Indices for Benzenoid Hydrocarbons

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In this report we studied the relationship between the vertex- and edge-connectivity indices, and the relationship of both these indices and the π-electron energies for benzenoid hydrocarbons. We also presented the use of edge-connectivity indices in the structure−boiling point modeling for benzenoid hydrocarbons. The obtained structure−boiling point models are compared with the models based on the vertex-connectivity indices and the distance-dependent molecular descriptors. The best structure−boiling point model for benzenoids achieved here is the quadratic model based on the edge-connectivity indices whose statistical characteristics are comparable to the best model from the literature; that is, Randić's model based on the multivariate regression analysis with the first-, second-, third-, and fourth-order geometric distance indices.

INTRODUCTION

This report was stimulated by two recent papers; namely, Randić's paper[1] on predicting boiling points of benzenoid hydrocarbons by the QSPR (quantitative structure−property relationship) technique based on the distance-dependent molecular descriptors, and Estrada's paper[2] introducing the edge-connectivity index. The edge-connectivity index appears to be a very promising topological index for QSPR/ quantitative structure−activity relationship (QSAR) studies.[2−5] Therefore, we decided to test the edge-connectivity index in the structure−boiling point modeling for benzenoid hydrocarbons and to compare the obtained models with the models based on the vertex-connectivity indices[6] and the models derived by Randić.[1] In addition, we also studied the relationship between the vertex- and edge-connectivity indices, and the relationship of both these connectivity indices and the π-electron energies of benzenoids.

DEFINITIONS OF CONNECTIVITY INDICES

The chemical graph theory[7,8] will be used because it simplifies the analysis. Thus, benzenoid hydrocarbons will be represented by benzenoid graphs. In Figure 1 we give a benzenoid graph B that corresponds to benzo(*e*)pyrene.

To review the connectivity indices, two particular graph theoretical concepts are needed; they are, the vertex-degree and the edge-degree concepts. The degree of a vertex v_i is equal to the number of adjacent vertices and is denoted by $d(v_i)$. Two vertices of a graph G are adjacent if there is an edge joining them. The degree of an edge e_k is equal to the number of adjacent edges and is denoted by $d(e_k)$. Two edges of a graph G are adjacent if they meet at the same
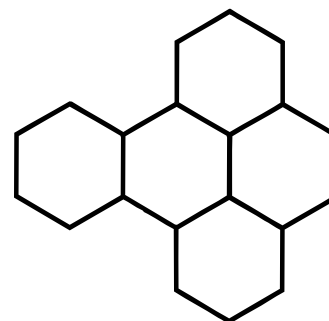
B

Figure 1. Benzenoid graph B depicting benzo(*e*)pyrene.

vertex. Because every edge in G connects two vertices, then the degree of edge e_k can be expressed in terms of degrees of its incident edges v_i and v_j by eq 1:

$$d(e_k) = d(v_i) + d(v_j) - 2 \qquad (1)$$

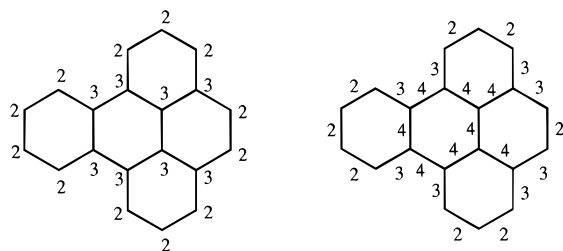In Figure 2 we give the vertex-degrees and edge-degrees of benzenoid graph B shown Figure 1.

Vertex-Connectivity Index. The vertex-connectivity index $\chi = \chi(G)$ of a (molecular) graph G was introduced by Randić in 1975:[6]

$$\chi = \sum_{\text{edges}} [d(v_i)\, d(v_j)]^{-1/2} \qquad (2)$$

where $d(v_i)$ is the vertex-degree and $[d(v_i)\, d(v_j)]^{-1/2}$ is the weight of the i−j edge.

For benzenoid graphs, eq 2 can be given in a closed form. Namely, in benzenoid graphs only two kinds of vertex-degrees appear; that is, vertices with degree 2 and vertices

Figure 2. The vertex-degrees (digits at each vertex) and edge-degrees (digits at each edge) of the benzo(*e*)pyrene graph.

with degree 3. This result gives rise to three edge-weights: $1/2 = 0.5$, $1/\sqrt{6} = 0.408$ and $1/3 = 0.333$. The numbers of corresponding edges are denoted as e_{22}, e_{23}, and e_{33}, respectively. Introducing these numbers and the corresponding weights into eq 2, we obtain:

$$\chi = 0.5e_{22} + 0.408e_{23} + 0.333e_{33} \qquad (3)$$

Therefore, all we need to compute the vertex-connectivity indices for benzenoid graphs is to enumerate their edge-types.

Edge-Connectivity Index. The edge-connectivity index $\epsilon = \epsilon(G)$ of a (molecular) graph G was introduced by Estrada.[2] This index is defined in the same way as the vertex-connectivity index, but uses edge-degrees $d(e_i)$ instead of vertex-degrees $d(v_i)$:

$$\epsilon = \sum_{\substack{\text{adjacent} \\ \text{edges}}} [d(e_i)\, d(e_j)]^{-1/2} \qquad (4)$$

where $[d(e_i)\, d(e_j)]^{-1/2}$ is the weight of adjacent edges e_i and e_j.

For benzenoid graphs, eq 4 can also be given in a closed form. In benzenoid graphs, three kinds of edge-degrees appear; that is, edges with degree 2, degree 3, and degree 4. These values give rise to five weights of adjacent edges: $1/2 = 0.5$, $1/\sqrt{6} = 0.408$, $1/3 = 0.333$, $1/2\sqrt{3} = 0.289$, and $1/4 = 0.25$. The numbers of adjacent edges with these weights are denoted as $n(2,2)$, $n(2,3)$, $n(3,3)$, $n(3,4)$ and $n(4,4)$, respectively. Introducing these numbers and the corresponding weights into eq 4, we obtain:

$$\chi = 0.5n(2,2) + 0.408\, n(2,3) + 0.33n(3,3) + \\ 0.289n(3,4) + 0.25n(4,4) \quad (5)$$

Therefore, all we need to compute the edge-connectivity indices for benzenoid graphs is to enumerate the numbers of adjacency edges and to classify them according to their weights.

RESULTS AND DISCUSSION

We computed the vertex- and edge-connectivity indices for 23 common benzenoid hydrocarbons. The values of these indices are given in Table 1 along with the π-electron energies in β units and boiling points in °C of considered benzenoids. The π-electron energies have been either taken from the tabulation of Coulson and Streiwieser[9] or computed by us. The experimental values of boiling points were taken from Basak *et al.*[10] The same set of benzenoid hydrocarbons, less pyrene, was also studied by Randić.[1]

Table 1. The Vertex-Connectivity Indices (χ), Edge-Connectivity Indices (ϵ), π-Electron Energies in β units (E_π), and Boiling Points (bp) °C of Studied Benzenoid Hydrocarbons

benzenoid hydrocarbon	χ	ϵ	E_π	bp
benzene	3.000	3.000	8.000	80.1
naphthalene	4.966	5.455	13.683	218.0
phenanthrene	6.950	7.926	19.448	338.0
anthracene	6.933	7.942	19.314	340.0
chrysene	8.933	10.247	25.192	431.0
benzanthracene	8.916	10.414	25.101	425.0
triphenylene	8.950	10.414	25.275	429.0
tetracene	8.899	10.430	25.188	440.0
benzo(*a*)pyrene	9.916	11.897	28.222	496.0
benzo(*e*)pyrene	9.933	11.897	28.336	493.0
perylene	9.933	11.897	28.245	497.0
anthanthrene	10.899	13.397	31.253	547.0
benzoperylene	10.916	13.379	31.425	542.0
dibenzo(*a,c*)anthracene	10.916	12.902	30.942	535.0
dibenzo(*a,h*)anthracene	10.899	12.885	30.881	535.0
dibenzo(*a,i*)anthracene	10.899	13.218	30.880	531.0
picene	10.915	12.868	30.943	519.0
coronene	11.899	14.863	34.572	590.0
dibenzo(*a,k*)pyrene	11.582	14.552	34.065	592.0
dibenzo(*a,h*)pyrene	11.566	14.385	33.928	596.0
dibenzo(*a,g*)pyrene	11.491	14.385	33.954	594.0
dibenzo(*a,d*)pyrene	11.915	14.390	34.031	595.0
pyrene	7.933	9.408	22.506	393.0
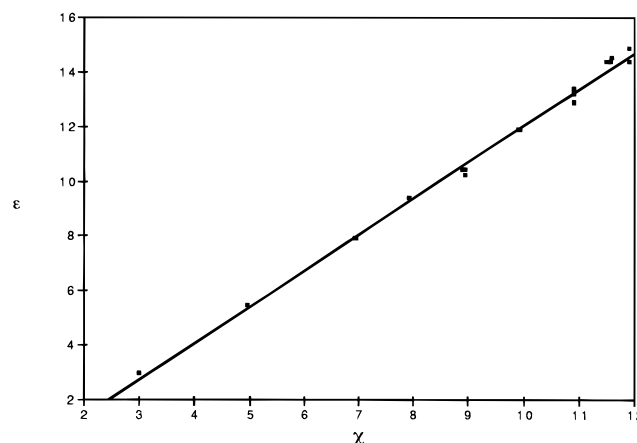
Figure 3. Plot of the edge-connectivity indices ϵ versus the vertex-connectivity indices χ for 23 benzenoid hydrocarbons.

Relationship between the Connectivity Indices for Benzenoids. We first considered the relationship between the vertex- and the edge-connectivity indices. A plot of the edge-connectivity indices against the vertex-connectivity indices for studied benzenoids is given in Figure 3.

The relationship between ϵ and χ, obtained by regression analysis, is:

$$\epsilon = 1.325(\pm 0.023)\chi - 1.227(\pm 0.225) \qquad (6)$$

$N = 23$; $r = 0.997$; $r^2(\text{adjusted}) = 0.993$; $s = 0.247$;
$$F = 3338; Q = 4.04$$

where N is the number of benzenoids, r is the correlation coefficient, $r^2(\text{adjusted})$ is the adjusted correlation coefficient, s is the standard error of estimate, F is the Fisher ratio, and Q is Pogliani's quality factor given by the ratio r/s.[11]

The high correlation between ϵ and χ is expected because they are closely related connectivity indices through eq 1. However, except for benzene they are not identical indices. All other benzenoid hydrocarbons possess different values
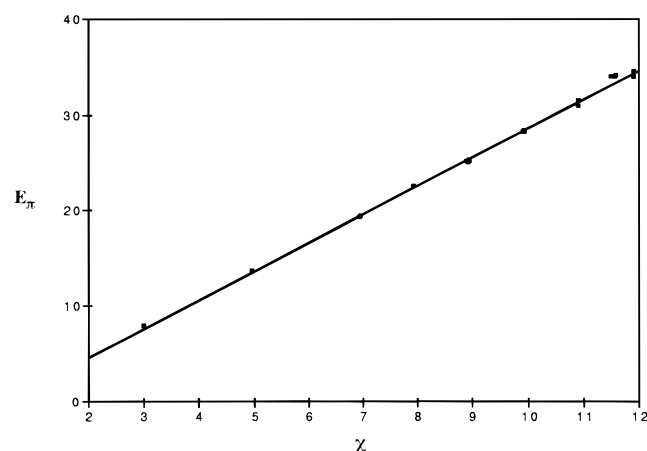
Figure 4. Plot of the π-electron energies E_π versus the vertex-connectivity indices χ for 23 benzenoid hydrocarbons.
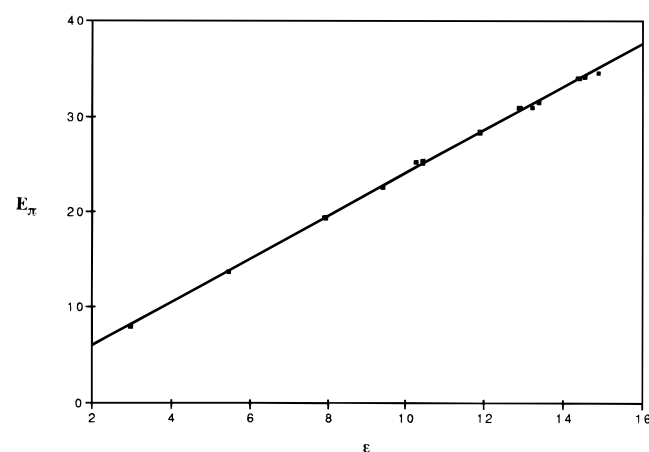
Figure 5. Plot of the π-electron energies E_π versus the edge-connectivity indices ϵ for 23 benzenoid hydrocarbons.

of ϵ and χ indices because different number of terms enter the formulae for computing ϵ and χ. For example, in the case of benzo(e)pyrene, 24 terms enter eq 3, (that is, $e_{22} = e_{23} = e_{33} = 8$) and 36 terms enter eq 5 [that is, $n(2,2) = 4$, $n(2,3) = 8$, $n(3,3) = 2$, $n(3,4) = 12$, and $n(4,4) = 10$].

Relationship between π-Electron Energies and Connectivity Indices for Benzenoid Hydrocarbons. We considered a linear relationships between π-electron energies E_π and connectivity indices. Plots between E_π and χ, and E_π and ϵ are shown in Figures 4 and 5, respectively.

The regression analysis gives the following relationships between E_π and connectivity indices:

$$E_\pi = 2.993(\pm 0.036)\chi - 1.323(\pm 0.349) \qquad (7)$$

$N = 23; r = 0.9986; r^2(\text{adjusted}) = 0.9970; s = 0.383; F = 6965; Q = 2.61$

$$E_\pi = 2.257(\pm 0.020)\epsilon + 1.486(\pm 0.229) \qquad (8)$$

$N = 23; r = 0.9993; r^2(\text{adjusted}) = 0.9984; s = 0.278; F = 3276; Q = 3.39$

The relationship between π-electron energies and vertex-connectivity indices of benzenoid hydrocarbons have been studied previously by several authors. Randić *et al.*[12] considered 30 randomly selected benzenoid hydrocarbons;

19 of these are also in our set. We repeated their statistical analysis and obtained the following relationship:

$$E_\pi = 2.944(\pm 0.022)\chi - 1.081(\pm 0.223) \qquad (9)$$

$N = 30; r = 0.9992; r^2(\text{adjusted}) = 0.9984; s = 0.282; F = 18379; Q = 3.54$

These results are somewhat better than our results given as eq 7.

Similar analysis, but on a much smaller set of benzenoid hydrocarbons, was also carried out earlier by Gupta and Singh[13] and Srivastava *et al.*[14] Both of these groups of authors considered the same set of nine benzenoid hydrocarbons, all of which are also in our set. Gupta and Singh[13] considered the relationship between the π-electron energies and the valence vertex-connectivity indices.[15] The valence vertex-connectivity index of benzenoids includes double bonds in the formula for computing the index. Thus, the vertices with degrees 2 and 3 become vertices with degrees 3 and 4, respectively. This relationship gives rise to following three edge-weights: $1/3 = 0.333$, $1/2\sqrt{3} = 0.289$, and $1/4 = 0.25$. The numbers of corresponding edges are denoted as e_{33}, e_{34} and e_{44}, respectively. Then the valence vertex-connectivity index for benzenoids is given by:

$$\chi^v = 0.333e_{33} + 0.289e_{34} + 0.250e_{44} \qquad (10)$$

The regression analysis produced the following relationship:

$$E_\pi = 0.763(\pm 0.839)\chi^v + 3.680(\pm 0.149) \qquad (11)$$

$N = 9; r = 0.9950; r^2(\text{adjusted}) = 0.9886; s = 0.805; F = 696; Q = 1.24$

Srivastava *et al.*[14] compared the π-electron energy of benzenoids obtained by a variant of the ω-HMO technique[16] and the valence vertex-connectivity indices. They obtained much better correlation than Gupta and Singh:[13]

$$E_\pi = 4.095(\pm 0.023)\chi^v - 0.287(\pm 0.135) \qquad (12)$$

$N = 9; r = 0.9999; r^2(\text{adjusted}) = 0.9998; s = 0.130; F = 33098; Q = 7.69$

Because the correlation obtained by Srivastava *et al.*[14] is so good and the one obtained by Gupta and Singh[14] is so disappointing, we repeated the Gupta-Singh analysis on the set of 30 benzenoid hydrocarbons that was considered by Randić *et al.*[12] The obtained results are comparable to those reported Srivastava *et al.*[14]:

$$E_\pi = 4.084(\pm 0.016)\chi^v - 0.271(\pm 0.113) \qquad (13)$$

$N = 30; r = 0.9998; r^2(\text{adjusted}) = 0.9996; s = 0.147; F = 67221; Q = 6.80$

All results just shown indicate that the π-electron energies of benzenoid hydrocarbons can be reproduced within a few percent by means of their (valence) vertex-connectivity
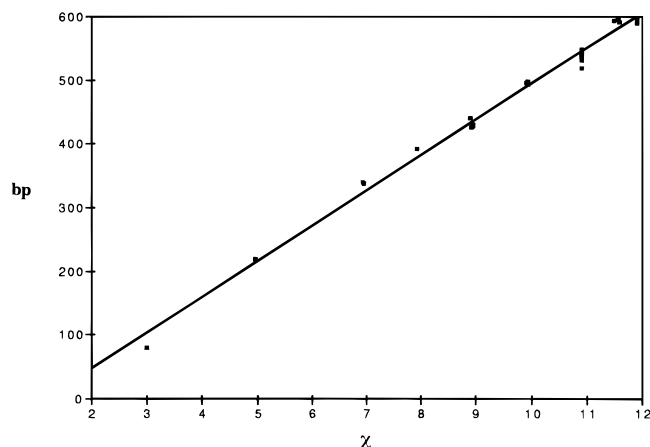
Figure 6. The linear correlation between the boiling points (bp) and the vertex-connectivity indices (χ) for 23 benzenoid hydrocarbons.
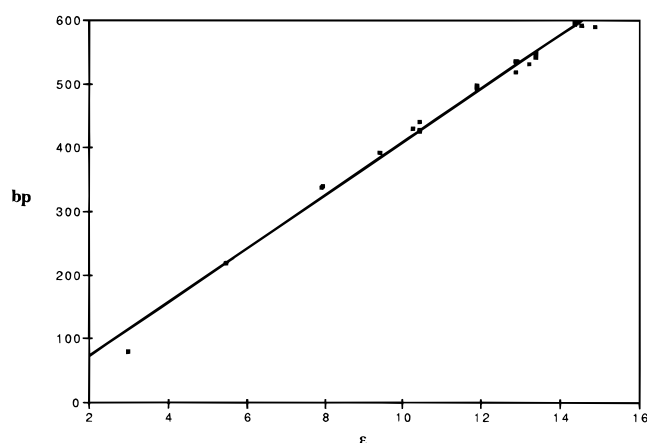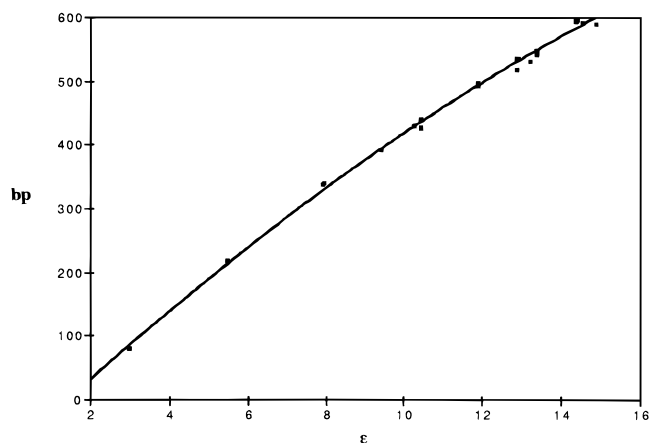

Figure 7. The linear correlation between the boiling points (bp) and the edge-connectivity indices (ϵ) for 23 benzenoid hydrocarbons.
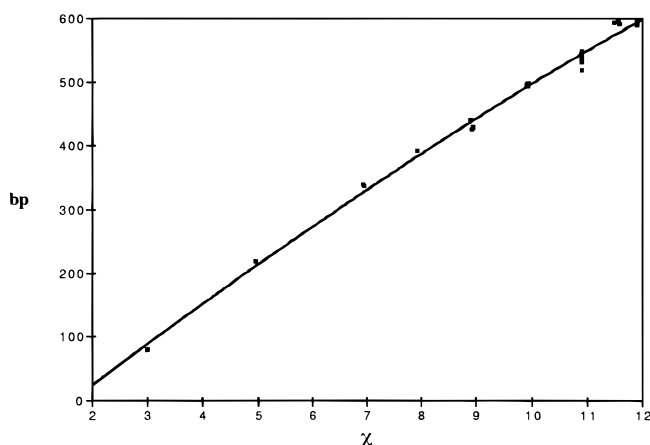
Figure 8. The quadratic correlation between the boiling points (bp) and the vertex-connectivity indices (χ) for 23 benzenoid hydrocarbons.

indices. Equation 8 shows that the same is also true for the edge-connectivity indices.

A Structure−Boiling Point Modeling for Benzenoid Hydrocarbons. In this section we consider linear and quadratic relationships between the boiling points, bp, and connectivity indices of benzenoids. The corresponding plots between bp and χ, and bp and ϵ are shown in Figures 6−9.

Figure 9. The quadratic correlation between the boiling points (bp) and the edge-connectivity indices (ϵ) for 23 benzenoid hydrocarbons.

The regression analysis gives the following relationships between boiling points (in °C) and connectivity indices for benzenoid hydrocarbons:

(i) Linear correlations:

$$bp = 55.821(\pm 1.167)\chi - 64.246(\pm 11.428) \quad (14)$$

$N = 23; r = 0.9954; r^2(\text{adjusted}) = 0.9905; s = 12.6; F = 2287; Q = 0.08$

$$bp = 41.996(\pm 0.882)\epsilon - 11.012(\pm 10.394) \quad (15)$$

$N = 23; r = 0.9954; r^2(\text{adjusted}) = 0.9904; s = 12.6; F = 2267; Q = 0.08$

(ii) Quadratic correlations:

$$bp = 68.202(\pm 6.563)\chi - 0.770(\pm0.402)\chi^2 - 108.450(\pm 25.487) \quad (16)$$

$N = 23; r = 0.9962; r^2(\text{adjusted}) = 0.9915; s = 11.9; F = 1290; Q = 0.08$

$$bp = 58.768 (\pm 2.986) \epsilon - 0.868 (\pm0.152) \epsilon^2 - 81.692 (\pm 13.998) \quad (17)$$

$N = 23; r = 0.9982; r^2(\text{adjusted}) = 0.9962; s = 8.0; F = 2859; Q = 0.12$

Equations 14−16 lead to similar predictions of the boiling points ($s = 12$ °C), but eq 17 gives the lowest value of the standard error ($s = 8$ °C). Because the boiling points of considered benzenoids range from 200 up to 600 °C (except for benzene), the errors range from 1 to 6%. This result indicates that the edge-connectivity index may be expected to do as well as the vertex-connectivity index in QSPR studies. There are to date only a few studies of this kind and they support the aforementioned statement.[2−5]

Our results compare favorably with Randić's analysis.[1] Randić's set of benzenoids has one member (pyrene) less

than the set considered by us. Randić reported several structure−boiling point relationships:

(i) Linear correlation between bp and χ:

$$bp = 55.011\chi - 59.801 \qquad (18)$$

$N = 22; r = 0.9964; s = 11.31, F = 2790; Q = 0.09$

(ii) Quadratic correlation between bp and χ:

$$bp = 71.161\chi - 0.998\chi^2 - 116.931 \qquad (19)$$

$N = 22; r = 0.9977; s = 9.32; F = 2058; Q = 0.11$

(iii) Linear correlation between bp and first-order geometric distance index ^1D:

$$bp = 6.871^1D + 97.2638 \qquad (20)$$

$N = 22; r = 0.9706; s = 32.27; F = 325; Q = 0.03$

(iv) Quadratic correlation between bp and first-order geometric distance index ^1D:

$$bp = 11.810^1D - 0.055\,(^1D)2 + 8.665 \qquad (21)$$

$N = 22; r = 0.9838; s = 24.70, F = 285; Q = 0.04$

(v) Multivariate regression analysis with first- and second-order geometric distance indices, ^1D and ^2D, respectively:

$$bp = 14.637^1D - 3.465^2D + 19.401 \qquad (22)$$

$N = 22; r = 0.9961; s = 12.07; F = 1224; Q = 0.08$

(vi) Multivariate regression analysis with first-, second-, third-, and fourth-order geometric distance indices, ^1D, ^2D, ^3D, and ^4D, respectively:

$$bp = 73.305^1D - 76.489^2D + 41.600^3D - 9.879^4D - 129.519 \qquad (23)$$

$N = 22; r = 0.9985; s = 7.88; F = 1443; Q = 0.13$

Note that the ^kD descriptors represent the average kth power of interatomic distances of a molecule suitably normalized.[1]

Statistical parameters of our eq 17: ($r = 0.9982; s = 8.0; F = 2859; Q = 0.12$) are comparable to the best Randić's model given as eq 23: ($r = 0.9985; s = 7.9; F = 1443; Q = 0.13$), but much less labor is required for computing the edge-vertex indices than the distance-dependent indices. This fact alone would then suggest the structure−boiling point model (eq 17) for the routine use.

CONCLUDING REMARKS

In this report it is shown that the vertex- and edge-connectivity indices are closely related molecular descriptors; that is, the edge-connectivity index can be computed from the vertex-connectivity index for benzenoids within the error of 2−5%. It is also shown that the π-electron energies of benzenoids can be computed quite accurately by means of either the vertex-connectivity indices or the edge-connectivity indices. The best model, presented as eq 13, gives the π-electron energies in β units of benzenoids within errors of <1%. The model based on the edge-connectivity indices,

eq 8, can predict the π-electron energies of benzenoids within errors of <2%.

We presented linear and quadratic structure−boiling point models based on either the vertex- or edge-connectivity indices of benzenoids and compared them with Randić's models. Our best structure−boiling point model is a quadratic model based on the edge-connectivity indices for which statistical parameters are comparable to those of the best Randić's model. Both models can predict the boiling points of benzenoid hydrocarbons within the error range 1−4%. This result indicates that for benzenoid hydrocarbons, the edge-connectivity indices can be used equally well as the geometric distance descriptors to account for variations of boiling points with structure.

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