Spectral Moments of Phenylenes

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In a series of publications Estrada (Estrada, E. *J. Chem. Inf. Comput. Sci.* **1996,** *36,* 844−849; **1997** *37,* 320−328; **1998,** *38,* 23−27) employed spectral moments of line graphs in QSPR and QSAR relationship studies of various classes of compounds. A recent paper (Marković, S.; Gutman, I. *J. Chem. Inf. Comput. Sci.* **1999,** *39,* 289−293) reported that in QSPR and QSAR investigations of benzenoid hydrocarbons based on linear combination of spectral moments, it made no difference whether one used spectral moments of the molecular graph or those of the line graph. In the present work spectral moments of molecular graphs (M_k's) and line graphs (μ_k's) of phenylenes are considered. The first few M_k's and μ_k's of phenylenes are dependent on identical structural parameters. It is proved that the two sets of moments of phenylenes are linearly dependent. It is also shown that in the case of the heat of formation of phenylenes there is no advantage in using lower spectral moments of line graphs instead of lower spectral moments of molecular graphs. In this way the redundancy observed in the case of benzenoid hydrocarbons is also shown to exist in the class of phenylenes.

1. INTRODUCTION

Phenylenes are a class of conjugated hydrocarbons composed of six- and four-membered rings, where the six-membered rings (hexagons) are adjacent only to four-membered rings, and every four-membered ring is adjacent to a pair of hexagons. Due to their aromatic and antiaromatic rings, phenylenes exhibit unique physicochemical properties. In Figure 1 some examples of phenylenes are presented. A phenylene containing h hexagons is called an [h]phenylene. It is assumed that the number of four-membered rings of an [h]phenylene amounts to $h - 1$, meaning that the structures in which alternating six- and four-membered rings are linked together in phenylenic super rings are not considered in the present paper.

The experimental chemistry of phenylenes is rapidly expanding, owing mainly to the work of Volhardt's research group. More information on the chemistry of phenylenes can be found in the reviews,[5,6] as well as in recent papers.[7−11] These discoveries in the experimental chemistry of phenylenes have challenged a great number of theoretical investigations.[4,12−19]

One of the main aims of theoreticians is to explain the dependence of various physicochemical properties of compounds on molecular structure. For this purpose graph theory is often employed. Concerning graph theory the molecules are represented by their molecular graphs. The molecular graph of a conjugated hydrocarbon is the graph representing the carbon atom skeleton of the corresponding molecule.

Consider a molecular graph **G** with n vertexes and m edges. The line graph of **G** (**L**) can be constructed in the following manner: a vertex of the line graph is associated to each edge of **G**. The edges of **L** are now obtained by connecting those vertexes of **L** which represent adjacent edges in **G**. In Figure 1 the phenylene examples are also presented by their corresponding molecular and line graphs. The molecular graphs of phenylenes are bipartite, whereas their line graphs are not, since they necessarily contain odd-membered rings.

The line graph has been discussed previously in chemical graph theory.[20,21] It was recently rediscovered[22] as an important source of graph theoretical invariants useful in the generation of new topological indices.[22−24]

Both **G** and **L** can be represented by their adjacency matrixes **A** and **E**, respectively. **A** is a square, symmetric matrix of order n whose elements $A(i,j)$ are equal to units and zeros, depending on whether the vertexes i and j are adjacent or not. **E** is also a square, symmetric matrix of order m. It is obvious that the elements $E(i,j)$ are equal to units if the edges i and j of **G** are adjacent. In other words, **A** reflects the adjacency of carbon atoms (existing of chemical bonds), whereas **E** reflects the adjacency of these bonds. Recall that the adjacency matrix of **L** is identical to the edge adjacency matrix of **G**.

The spectral moments of **G** and **L** are defined as $M_k = \text{Tr}[A^k]$ and $\mu_k = \text{Tr}[E^k]$, respectively, where Tr denotes the traces of the matrixes **A** and **E**. Structural interpretation of spectral moments is as follows: M_k and μ_k are equal to the numbers of self-returning walks of length k contained in molecular and line graphs, respectively.

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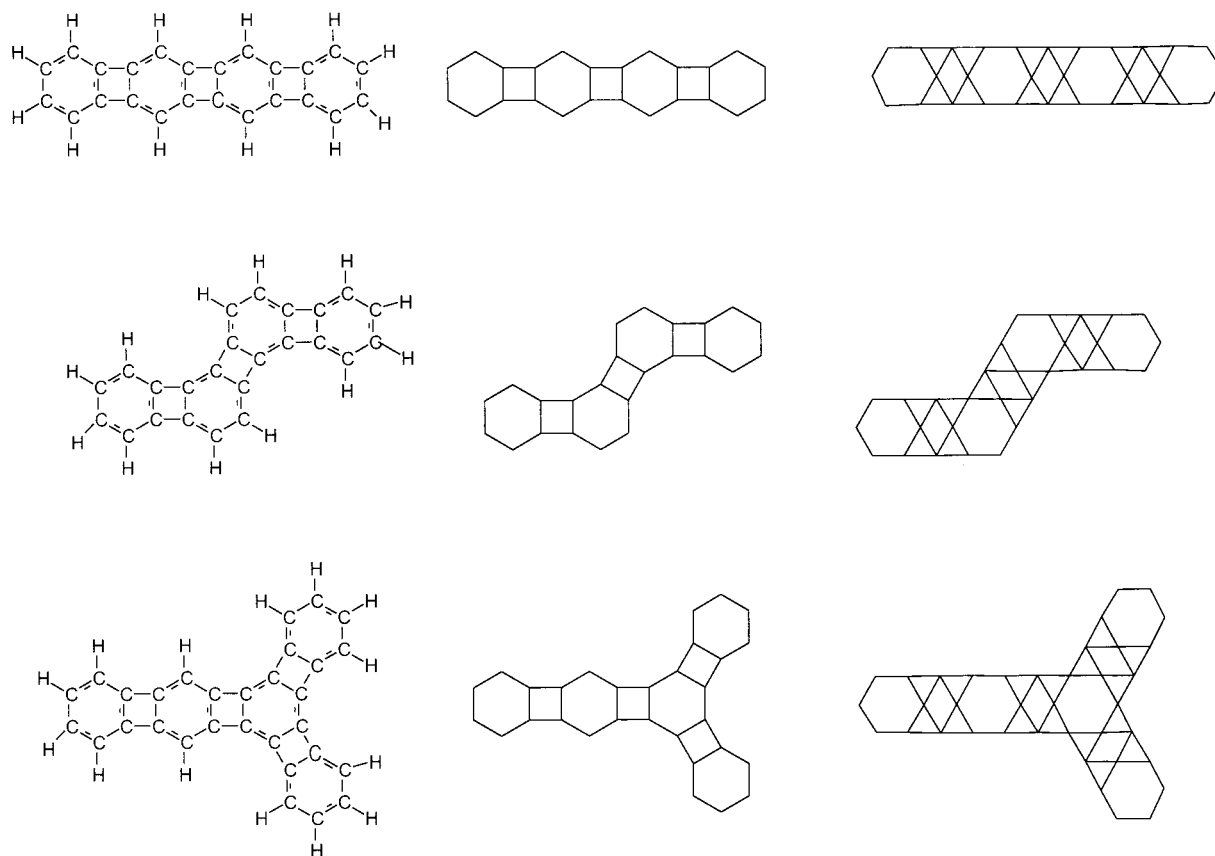
SPECTRAL MOMENTS OF PHENYLENES

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Figure 1. Some examples of phenylenes presented by their structural formulas and corresponding molecular and line graphs.

The spectral moments of molecular graphs have found remarkable applications both in the physical chemistry of the solid state[25-27] and in the theoretical chemistry of conjugated molecules.[17,19,28-40] In all applications of spectral moments it is necessary to know how they depend on molecular structure. For this reason, efforts have been made to establish topological formulas for spectral moments of various classes of molecular graphs. Particular attention has been devoted to benzenoid hydrocarbons,[31-33,37-39] acyclic polyenes,[30] and phenylenes.[17,19] Since every self-returning walk embraces a certain structural fragment of the molecular graph, it is possible to express M_k as a linear combination of the numbers of these fragments. For phenylenes the expressions for the first few spectral moments can be significantly simplified. Thus, for a phenylene with h hexagons

$$M_0 = 6h \tag{1}$$

$$M_2 = 16h - 4 \tag{2}$$

$$M_4 = 80h - 44 \tag{3}$$

$$M_6 = 484h - 352 + [6b] \tag{4}$$

$$M_8 = 3136h - 2636 + [128b + 16h_{A_3}] \tag{5}$$

$$M_{10} = 20976h - 19504 + [1680B + 3370C + 5060F + 6750G + 580h_{A_3}] \tag{6}$$

Formulas 1–5 have been previously described.[17] The M_{10}

of phenylenes (eq 6) has been recently evaluated.[19] The notation used in the equations above will be explained below.

Investigations concerning the spectral moments of line graphs have commenced relatively recently. In a series of papers Estrada employed these spectral moments in quantitative structure–property (QSPR) and quantitative structure–activity (QSAR) relationship studies. For this purpose, the spectral moments of L were expressed in terms of structural fragments of molecules, and then they were used to describe some physicochemical properties of alkanes,[1] boiling points of alkyl halides,[2] antifungal activity of benzyl alcohols,[2] and boiling points of cycloalkanes.[3] These expressions for spectral moments of the line graphs will be further called Estrada's expressions.

In a recent paper[41] the spectral moments of the iterated line graph sequence (ILGS) are defined and expressed in terms of structural fragments of molecular graphs, i.e., embedding frequencies. This QSPR model is used to describe some physicochemical properties of alkanes.

2. SPECTRAL MOMENTS OF THE LINE GRAPHS OF PHENYLENES

Estrada's Expressions. Estrada's expressions for spectral moments of line graphs can be applied to any class of molecular graphs. If the spectral moments of nonweighted graphs are considered up to seventh order, there are 12 acyclic and 53 cyclic fragments which contribute to the moments. In the special case of phenylenes this problem is reduced to the molecular fragments depicted in Figure 2.
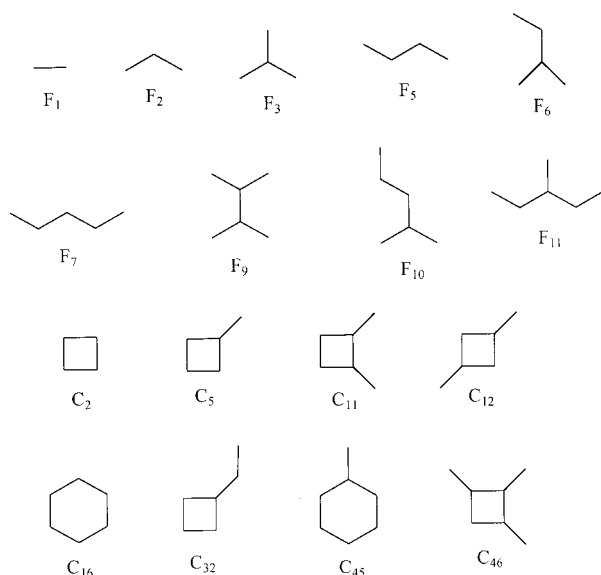
Figure 2. Molecular graph fragments relevant for Estrada's expressions for the spectral moments of line graph of phenylenes.

Estrada's formulas for spectral moments of the line graphs of phenylenes read as follows:

$$\mu_0 = |F_1| \tag{7}$$

$$\mu_2 = 2|F_2| \tag{8}$$

$$\mu_3 = 6|F_3| \tag{9}$$

$$\mu_4 = 2|F_2| + 12|F_3| + 4|F_5| + 8|C_2| \tag{10}$$

$$\mu_5 = 30|F_3| + 10|F_6| + 10|C_5| \tag{11}$$

$$\mu_6 = 2|F_2| + 60|F_3| + 12|F_5| + 24|F_6| + 6|F_7| + 24|F_9| + 72|C_2| + 24|C_5| + 12|C_{11}| + 12|C_{12}| + 12|C_{16}| \tag{12}$$

$$\mu_7 = 126|F_3| + 84|F_6| + 112|F_9| + 14|F_{11}| + 154|C_5| + 56|C_{11}| + 56|C_{12}| + 14|C_{32}| + 14|C_{45}| \tag{13}$$

Since the line graphs of phenylenes necessarily contain triangles (Figure 1), their odd spectral moments, except μ_1, are nonzero.

In these formulas the numbers of molecular fragments F$_x$ and C$_x$ are denoted by $|F_x|$ and $|C_x|$, respectively. Some structural fragments, such as F$_1$, F$_3$, C$_2$, and C$_{16}$, can be easily recognized in the molecular graph of an arbitrary phenylene. The counts of these fragments can be also determined in a simple way (see the text below). On the other hand, the enumeration of some other fragments is a fatiguing combinatorial task.

Topological Formulas. In this paper combinatorial formulas for spectral moments (up to μ_9) of the line graphs of phenylenes are designed. These expressions depend on six mutually independent invariants that can be easily deduced from molecular graphs of phenylenes.

Before presenting our main results, i.e., combinatorial formulas for μ_k, we have to determine some structural details and to fix our notation. We follow the terminology that was originally suggested for benzenoid hydrocarbons[42] and then applied to phenylenes.[17,19] Hence, h stands for the number of hexagons of phenylenes. There are four types of hexagons
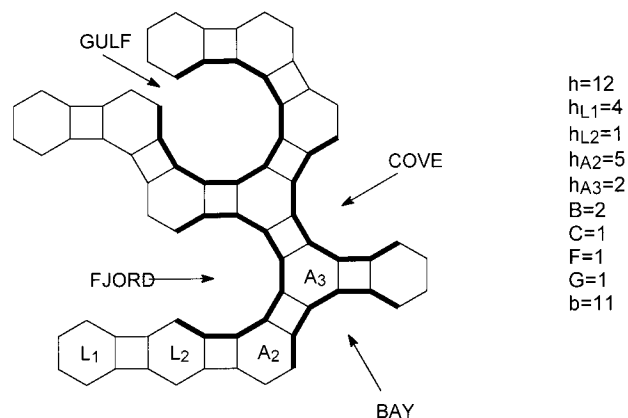

Figure 3. An example of phenylenes illustrating structural details and their counts relevant for the topological expressions for the spectral moments of line graph of phenylenes.

in phenylenes that can be distinguished with respect to their mutual position: L$_1$, L$_2$, A$_2$, and A$_3$. Their definition is clear from a self-explanatory example given in Figure 3. h_{L_1}, h_{L_2}, h_{A_2}, and h_{A_3} represent the numbers of hexagons of types L$_1$, L$_2$, A$_2$, and A$_3$, respectively. In Figure 3 some structural details of the perimeter of phenylenes are also indicated: a bay, cove, fjord, and gulf. The numbers of such fragments are denoted by B, C, F, and G, respectively. Then the number of bay regions (b) is determined as $b = B + 2C + 3F + 4G$.

It is obvious that

$$\mu_0 = m = 8h - 2 \quad \text{and}$$
$$\mu_1 = 0 \tag{14}$$

In addition to this, we deduced following formulas for spectral moments of the line graphs of phenylenes:

$$\mu_2 = 28h - 16 \tag{15}$$

$$\mu_3 = 24h - 24 \tag{16}$$

$$\mu_4 = 180h - 144 + [4b] \tag{17}$$

$$\mu_5 = 360h - 360 + [20b] \tag{18}$$

$$\mu_6 = 1600h - 1480 + [108b + 12h_{A_3}] \tag{19}$$

$$\mu_7 = 4480h - 4536 + [504b + 56h_{A_3}] \tag{20}$$

$$\mu_8 = 16708h - 16608 + [2268B + 4544C + 6820F + 9096G + 416h_{A_3}] \tag{21}$$

$$\mu_9 = 53160h - 55176 + [9792B + 19656C + 29520F + 39384G + 2268h_{A_3}] \tag{22}$$

Formulas 15−22 were designed on the basis of earlier experience gained by studying M_k and μ_k of benzenoid hydrocarbons. That is, on the basis of considerations similar to what has been used in the refs 37 and 4, a theorem may be applied which states that for any given value of k, μ_k increases with increasing size of the molecular graphs of phenylenes, at most as a linear function of h. This means that μ_k can be presented as

$$\mu_k = Ah + B + r_k \tag{23}$$

Here, A and B are the constants (depending on k), whereas

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r_k stands for the residual embracing the effects of all other structural factors on the respective μ_k. The parameters A and B in eq 23 were determined by means of a few selected examples of linear phenyenes. Then the form of r_k was found out. As expected, r_k was numerically much smaller than $Ah + B$ (for example, $r_k = 0$ for $k = 0$, 2, and 3). That finding much simplified the investigation of topological formulas for spectral moments of line graphs of phenylenes. In eqs $17 - 22$ the residuals r_k are indicated by square brackets. In all cases examined r_k is divisible by k.

Equations 15−22 were checked on a large number of examples, including all possible types of phenylenes. The final form of the combinatorial formulas for μ_k should be proved in a rigorous mathematical manner.

Equations 7−13 Are Equivalent to Equations 14−20. Both Estrada's and the approach of this investigation show that the spectral moments of line graphs can be expressed in terms of counts of certain fragments of molecular graphs of phenylenes. At the first glance, eqs 7−13 are quite different from eqs 14−20. Nevertheless, it is proved that they are mutually equivalent.

As stated above, some of Estrada's fragments can be enumerated in a simple way. For example, $|F_1| = m$; $|F_3| =$ number of vertexes of degree 3 (n_3); $|C_2| =$ number of four-membered rings (h_4); $|C_{16}| =$ number of hexagons of molecular graph. On the basis of this, the following expressions may be deduced:

$$|F_1| = 8h - 2 \tag{24}$$

$$|F_3| = 4h - 4 \tag{25}$$

$$|C_2| = h - 1 \tag{26}$$

$$|C_{16}| = h \tag{27}$$

In addition to this, we prove that the following formulas are also fulfilled:

$$|F_2| = 14h - 8 \tag{28}$$

$$|F_5| = 24h - 18 + b \tag{29}$$

$$|F_6| = 20h - 20 + 2b \tag{30}$$

$$|F_7| = 36h - 32 + 4b + 2h_{A_3} \tag{31}$$

$$|F_9| = 4h - 4 + b \tag{32}$$

$$|F_{10}| = 24h - 28 + 6b + 4h_{A_3} \tag{33}$$

$$|F_{11}| = 28h - 28 + 8b \tag{34}$$

$$|C_5| = 4h - 4 \tag{35}$$

$$|C_{11}| = 4h - 4 \tag{36}$$

$$|C_{12}| = 2h - 2 \tag{37}$$

$$|C_{32}| = 4h - 4 + 2b \tag{38}$$

$$|C_{45}| = 4h - 4 \tag{39}$$

$$|C_{46}| = 4h - 4 \tag{40}$$

By substituting the eqs 24−40 back into eqs 7−13, the formulas 14−20 are easily calculated.
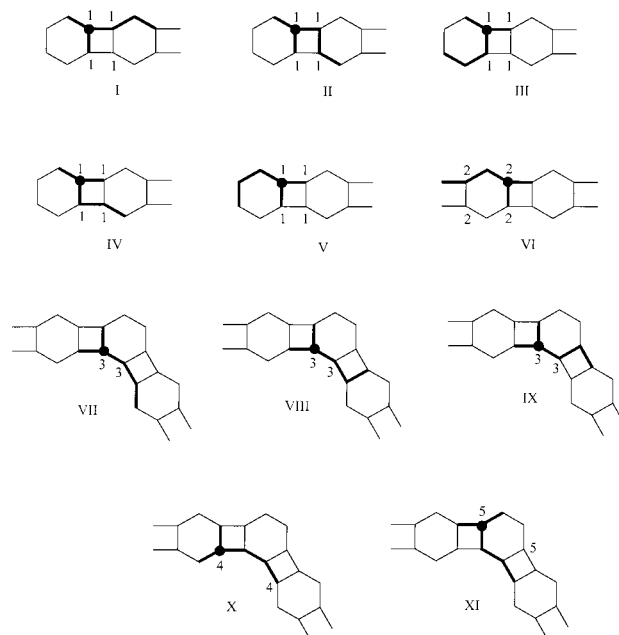

Figure 4. Possible arrangements of the F_{10} fragment in the molecular graph of a phenylene.

The details concerned with evaluation of eqs 33 and 38 are presented as an example (Figure 4).

As shown in Figure 2, an F_{10} fragment possesses a vertex of degree 3, which may be understood as its central point. In Figure 4 such vertexes are represented by heavy dots; the analogous vertexes are represented by identical numbers. Attention should be paid to an arbitrary vertex of degree 3 (heavy dot 1). Note that such a vertex can belong to hexagons of all types, including those of L_1 type. This vertex obviously provides five F_{10} fragments (structures I−V), each of them being spread over only one four-membered ring and one or two hexagons. The hexagons of other types provide vertexes of degree 3, which are the central points for additional F_{10} fragments embracing two four-membered rings and one or two hexagons. In Figure 4, structure VI shows the F_{10} fragment whose central point (2) is located at the L_2-type hexagons. Finally, heavy dots 3−5 in structures VII−XI are the central points of F_{10} fragments lying in the bay regions, i.e., belonging to A_2- and A_3-type hexagons.

Phenylenes obviously possess $(h - 1) \times 4$ vertexes of type 1, $4h_{L_2}$ vertexes of type 2; and $10h_{A_2} + 30h_{A_3}$ vertexes of types 3−5. On the basis of this consideration we can write

$$|F_{10}| = (h - 1)(20) + 4h_{L_2} + 10h_{A_2} + 30h_{A_3}$$

Taking into account that $h_{L_1} = h_{A_3} + 2$, $b = h_{A_2} + 3h_{A_3}$, and $h = h_{L_1} + h_{L_2} + h_{A_2} + h_{A_3}$, eq 33 is easily obtained.

It is clear from Figure 2 that a four-membered ring of phenylenes is the central part of the C_{32} fragment. Figure 5 reveals that each four-membered ring is the central part of four C_{32} fragments (structures I−IV). In the case of phenylenes $h_4 = h - 1$ ($4h - 4$ C_{32} fragments provided by them). An additional C_{32} fragment, embracing two four- and one six-membered rings, is spread over a bay region (structure V). Each bay region obviously provides two analogous four-membered rings, both denoted by unity in Figure 5 ($2b$ C_{32} fragments). Following this consideration eq 38 can be calculated.

Table 1. Data Showing the Quality of the Approximations 41 and 42: Correlation Coefficients (R), Average Relative Errors (ARE), Sample Dispersions (SD), and Results of the F-test (f)

		eq 41					eq 42		
p	R	ARE (%)	10^2SD	f	q	R	ARE (%)	10^2SD	f
0	0.999 2	0.97	2802.55		0	0.999 2	0.97	2802.55	
6	0.999 97	0.19	105.63	13.25	4	0.999 97	0.19	105.63	13.25
8	0.999 97	0.17	92.92	0.57	6	0.999 97	0.17	92.92	0.57
10	0.999 98	0.16	71.65	0.65	8	0.999 98	0.16	71.65	0.65
12	0.999 98	0.14	67.19	0.53	10	0.999 98	0.14	67.19	0.53
14	*0.999 998*	*0.05*	*6.62*	*5.06*	*11*	*0.999 998*	*0.05*	*5.51*	*6.09*
16	0.999 998	0.05	6.11	0.54	12	0.999 998 6	0.04	4.62	0.60
18	0.999 998 6	0.04	4.86	0.63	13	0.999 998 8	0.04	4.18	0.55
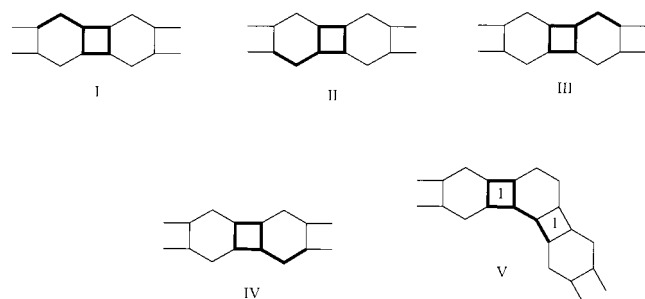
Figure 5. Possible arrangements of the C_{32} fragment in the molecular graph of a phenylene.

Comparing Spectral Moments of Molecular and Line Graphs of Phenylenes. By inspecting Eq 1−6 and 15−22, it can be concluded that precisely the same structural invariants determine the first few spectral moments of both the molecular and line graphs of phenylenes (similar to the case of benzenoid hydrocarbons). In particular, $\mu_0-\mu_3$ and M_0-M_4 depend solely on the number of hexagons. The situation is analogous with μ_4, μ_5, and M_6: they are all determined by h and b. Then, μ_6, μ_7, and M_8 are expressed in terms of h, b, and h_{A_3}. Finally, μ_8, μ_9, and M_{10} are expressed in terms of h, h_{A_3}, B, C, F, and G. All mentioned dependencies are linear, suggesting that the spectral moments of the two graphs can also be linearly dependent, implying, in turn, that expressing some physicochemical property of phenylenes as a linear combination of lower μ_k's or of lower M_k's would yield identical or very similar results. To investigate whether there is any advantage in using spectral moments of the line graph instead of the spectral moments of the molecular graph, the heat of formation (ΔH_f) of phenylenes was explored.

3. APPROXIMATING THE HEAT OF FORMATION OF PHENYLENES IN TERMS OF SPECTRAL MOMENTS OF MOLECULAR AND LINE GRAPHS

The results of investigation of the dependence of ΔH_f of phenylenes on both spectral moments of **G** and **L** are reported below. The aim is to show whether there is any advantage when using μ_k instead of M_k. For this purpose ΔH_f is approximated by means of the polynomials

$$\Delta H_f = a_0 M_0 + a_2 M_2 + ... + a_p M_p + a_{p+2}$$
$$p = 0, 2, 4, ..., 18 \quad (41)$$

$$\Delta H_f = b_0 \mu_0 + b_2 \mu_2 + b_3 \mu_3 + ... + b_q \mu_q + b_{q+1}$$
$$q = 0, 2, 3, ..., 13 \quad (42)$$

As already mentioned, all odd spectral moments of molecular

graphs, as well as μ_1, are equal to zero in the case of phenylenes. For this reason, p in eq 41 is necessarily even, and the term $b_1\mu_1$ in eq 42 is ignored.

Calculations were performed on the set which was obtained as follows: 49 catacondensed benzenoids were selected from the standard set of 106 benzenoid hydrocarbons.[43] On the basis of these benzenoid hydrocarbons corresponding phenylenes were constructed. Molecular graphs of these compounds are depicted in the Appendix.

Computational Methods. The structures of 49 phenylenes were generated by PC MODEL, version 7.00,[44] which involves an MMX force field,[45] and were saved as MOPAC files[46] for MNDO-PM3 semiempirical calculations. In our work we used the PM3 method, which proved to be highly reliable for investigating molecular properties of conjugated compounds. We used the MOPAC program package, version 7.01. The geometries of all molecular structures correspond to the energy minima in a vacuum. When needed, obtained structures were refined by Bartel's method (nonlinear least squares gradient minimization routine−NLLSQ).

The coefficients a_0, a_2, ..., a_{p+2}, as well as b_0, b_2, b_3, ..., b_{q+1}, were determined by the least squares fitting for different values of p and q, and can be obtained from the authors upon request. The correlation coefficients, average relative errors, and sample dispersions for eqs 41 and 42 were also calculated. These results, showing the qualities of the approximations 41 and 42, are presented in Table 1, except those where linear dependency was encountered (see the text below).

The introduction of a new fitting parameter a_p into (41) or b_q into (42) necessarily increased the correlation coefficients and decreased the average errors and sample dispersions. To check if this improvement was statistically significant or not, the standard F-test was used.[47] The results of the F-test are presented in Table 1. The quantity f for eq 41 is equal to the ratio of the sample dispersion for a certain p and that for $p + 2$, divided by the respective value of the F-distribution, at the confidence level of 99%. Therefore, if f is (much) greater than unity, then the change $p \to p + 2$ significantly improves the quality of the respective approximation and is justified; if f is below (or slightly above) unity, then, from a statistical point of view, the previous and new equations are equivalent, and preference should be given to the former one (because it has fewer empirical parameters). The quantity f for eq 42 is defined analogously.

Discussion. By inspecting eqs 1−3, one can conclude that M_2 is linearly dependent on M_0, and M_4 is linearly dependent on M_0 and M_2. Consequently, $p = 0 \to p = 2$, as well as $p = 2 \to p = 4$, will not cause any advantage in the accuracy

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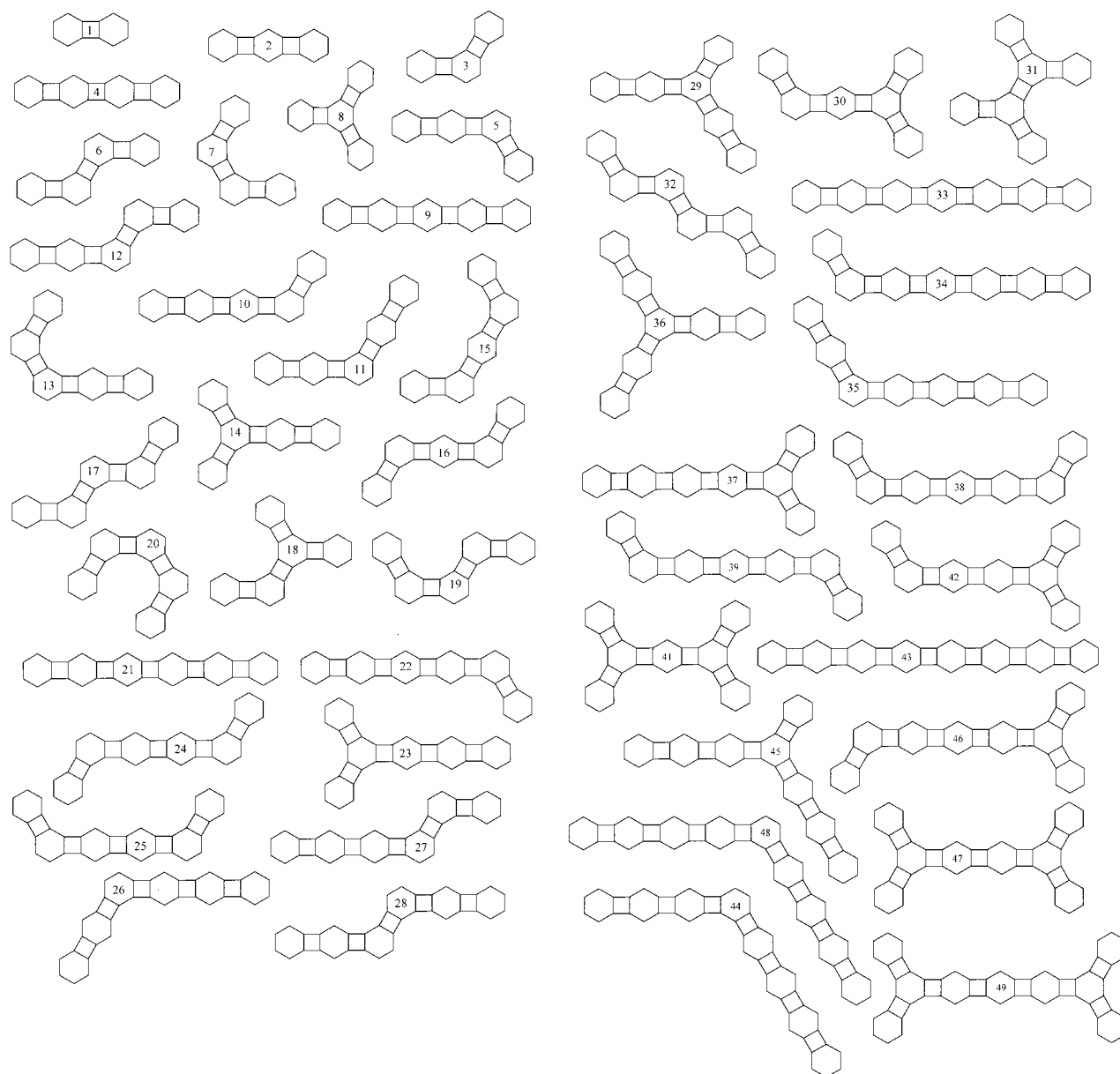*J. Chem. Inf. Comput. Sci., Vol. 41, No. 1, 2001* **117**

Figure 6. Molecular graphs of phenylenes considered in this paper.[43] For details see the text.

of eq 41, meaning that the correlation coefficients, average relative errors, and sample dispersions will remain completely unchanged. From eqs 14−16 we can similarly conclude that μ_2 is linearly dependent on μ_0, and μ_3 is linearly dependent on μ_0 and μ_2. Therefore, $q = 0 \rightarrow q = 2$, as well as $q = 2 \rightarrow q = 3$, does not affect the accuracy of eq 42. For this reason, the respective data concerning eqs 41 and 42 are not given in Table 1.

By increasing the parameters p and q, the accuracies of eqs 41 and 42 are necessarily enhanced, meaning that the correlation coefficients are increased, whereas the relative average errors and sample dispersions are decreased. For the first few values of p and q the qualities of approximations significantly increase, until the relative errors fall below 0.05% and correlation coefficients exceed the value of 0.999 99. With further increasing the values of p and q these improvements fade, and for $p > 18$ and $q > 13$ they become irrelevant.

One can notice that the sample dispersions for $p = 0$, 6, 8, 10, and 12 in eq 41 are identical to those for $q = 0$, 4, 6,

8, and 10 in eq 42, respectively. This means that we can achieve the same quality of approximation for ΔH_f of phenylenes by using, for example, either $\Delta H_f \approx a_0 M_0 + a_6 M_6 + a_8 M_8 + a_{10} M_{10} + a_{12}$ or $\Delta H_f \approx b_0 \mu_0 + b_4 \mu_4 + b_6 \mu_6 + b_8 \mu_8 + b_9$. The advantage of the formula 42 over eq 41 is that, at the same accuracy, it requires the moments of lower orders. It is also revealed that M_0 (or M_2 or M_4) and μ_0 (or μ_2 or μ_3), M_6 and μ_4 (or μ_5), M_8 and μ_6 (or μ_7), and M_{10} and μ_8 (or μ_9) are mutually linearly dependent. On the basis of the sample dispersions for $p = 12$ and $q = 10$, we can suppose that M_{12} and μ_{10} are also linearly dependent and, therefore, yield identical results in the spectral-moment expansion of ΔH_f of phenylenes. In the cases of higher moments ($p \geq 14$; $q \geq 11$) eqs 41 and 42 give different but very similar results, which are slightly better for eq 42. Thus, the preference can be given to eq 42.

Both eqs 41 and 42 are surprisingly good approximations for ΔH_f of phenylenes. Furthermore, they in some way elucidate the dependence of ΔH_f of phenylenes on their structure. When only M_0 or μ_0 are used in the spectral-

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moment expansion, the relative error is less than 1%, which confirms that the major part of ΔH_f (more than 99%) is determined by the size of the molecules, expressed by the number of hexagons. Bearing in mind that for phenylenes $n = 6h$, the previous statement also implies that more than 99% of ΔH_f is determined by the number of carbon atoms. On introducing M_6 into (41), as well as μ_4 (or μ_5) into (42), the qualities of the approximations are drastically improved. This is clearly revealed by the results of F-test, yielding 13.25 in both cases. On the basis of this we can conclude that the number of bay regions, structural features influencing M_6, μ_4, and μ_5, plays a significant role in the dependence of ΔH_f on molecular topology of phenylenes. According to the F-test, significant improvements of the approximations are also achieved for $p = 12 \rightarrow p = 14$ or, analogously, for $q = 10 \rightarrow q = 11$. These approximate formulas reproduce ΔH_f of phenylenes with the accuracy of about 99.95%. Unfortunately, the dependencies of M_{14} and μ_{11} on molecular structure of phenylenes have not been elucidated. For this reason we cannot distinguish structural details of phenylenes whose contribution to ΔH_f is significant.

4. CONCLUDING REMARKS

In the present work, combinatorial formulas for the spectral moments of the line graph of phenylenes up to the ninth power are created. These expressions show that μ_k's of phenylenes depend on topological invariants that can be easily deduced from the molecular graph: h, h_{A_3}, B, C, F, and G. Similarly, as in the case of benzenoid hydrocarbons, the first few M_k's and μ_k's of phenylenes are dependent on identical structural parameters. Furthermore, the two sets of moments are mutually linearly dependent in the case of phenylenes. On the basis of this fact, it can be predicted that expressing some physicochemical property of phenylenes as a linear combination of lower μ_k's or of lower M_k's would yield identical or very similar results. To elucidate this question, the heat of formation of phenylenes is approximated in terms of spectral moments of both **A** and **E** matrices. Both approximations yield surprisingly good results and indicate structural features that influence ΔH_f of phenylenes. On the other hand, there is no advantage in using lower spectral moments of the line graph, instead of lower spectral moments of the molecular graph. In this way it is demonstrated that the redundancy observed in the case of benzenoid hydrocarbons also exists in the class of phenylenes: in QSPR and QSAR investigations of benzenoid hydrocarbons and phenylenes, based on the spectral-moments expansion, it does not make any difference if one uses the **A** or **E** matrix. This conclusion may not be generalized to QSPR and QSAR studies of all classes of compounds, particularly those whose molecular structure diverges significantly from that of benzenoids and phenylenes.

ACKNOWLEDGMENT

APPENDIX

Figure 6 shows the molecular graphs of the phenylenes considered in this paper. Table 2 lists the heats of formation of these compounds.

Table 2. Heats of Formation of the Phenylenes Presented in Figure 6

no.	ΔH_f (kcal/mol)	no.	ΔH_f (kcal/mol)	no.	ΔH_f (kcal/mol)
1	109.83	**18**	358.39	**34**	541.32
2	196.64	**19**	360.44	**35**	540.14
3	193.05	**20**	359.99	**36**	531.95
4	283.93	**21**	458.70	**37**	534.74
5	279.36	**22**	453.93	**38**	536.57
6	276.76	**23**	447.39	**39**	536.56
7	276.81	**24**	449.23	**40**	539.98
8	274.28	**25**	449.23	**41**	524.12
9	371.31	**26**	452.78	**42**	530.07
10	366.57	**27**	450.39	**43**	633.86
11	365.58	**28**	449.58	**44**	628.10
12	363.16	**29**	446.12	**45**	620.98
13	363.20	**30**	443.12	**46**	617.38
14	360.23	**31**	440.22	**47**	610.90
15	362.18	**32**	444.06	**48**	715.71
16	362.18	**33**	546.14	**49**	698.32
17	360.44				

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