Calculating the Determinant of the Adjacency Matrix and Counting Kekulé Structures in Circulenes

I. Gutman [a], Y.-N. Yeh [b], S.-L. Lee [c], H. Hosoya [d], and S. J. Cyvin [e]

[a] Institute of Physical Chemistry, Attila József University, Szeged, Hungary; on leave from Faculty of Science, University of Kragujevac
[b] Institute of Mathematics, Academia Sinica, Taipei, Taiwan, R.O.C.
[c] Department of Chemistry, National Chung-Cheng University, Chia-Yi, Taiwan, R.O.C.
[d] Department of Information Sciences, Ochanomizu University, Tokyo, Japan
[e] Division of Physical Chemistry, University of Trondheim, Trondheim, Norway

Z. Naturforsch. **49a,** 1053–1058 (1994); received April 12, 1994

The determinant of the adjacentcy matrix, the algebraic structure count and the Kekulé structure count of circulenes are shown to conform to simple expressions containing Fibonacci numbers.

Introduction

Whereas the investigation of the topological properties of benzenoid and coronoid hydrocarbons seems to be a very active and prolific field of research in contemporary mathematical chemistry [1–5], non-benzenoid conjugated systems have been studied to a much lesser extent. Little is known about the Kekulé structures of non-benzenoids, especially when compared with the plethora of such results obtained for benzenoids and coronoids [1–3]. In order to fill this gap we have recently undertaken a systematic study of non-benzenoid molecules and their Kekulé structures. In this paper we report our findings for circulenes, a class of conjugated species that were not included among coronoid hydrocarbons because of some formal classification criteria [4].

The molecule of n-circulene is composed of n hexagons, arranged so as to form an n-membered inner and a $(3n)$-membered outer perimeter. Its molecular graph will be denoted by Γ_n.

The 6-circulene is just the long-known benzenoid hydrocarbon coronene. The other members of the circulene family that have been obtained so far are 5-circulene (or corannulene) [6], and 7-circulene [7]; for synthetic work directed towards 8-circulene see [8].

If n is even then n-circulene is an alternant hydrocarbon. Its algebraic structure count (ASC) is then given by [9–11]

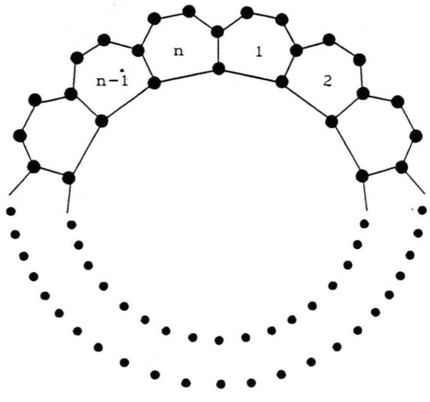
$$\mathrm{ASC}\{\Gamma_n\} = \sqrt{\det A(\Gamma_n)}\,, \tag{1}$$

where $\det A(\Gamma_n)$ is the determinant of the adjacency matrix of the molecular graph Γ_n.

If n is odd, then the n-circulene is non-alternant and its algebraic structure count is not defined; in this case the right-hand side of (1) needs not be integer-valued.

Recall that the ASC-concept is based on a certain "parity" that can be assigned to every Kekulé structure. Then ASC is just the difference between the number of "even" and "odd" Kekulé structures [9–11]. An alternative name proposed for algebraic structure count is "corrected structure count" [12, 13].

Alternant hydrocarbons have well-defined ASC-values. In some non-alternant hydrocarbons, on the other hand, it is not possible to consistently assign parities to Kekulé structures [14, 15], and then the ASC-concept becomes meaningless. The odd circulenes may serve as typical examples of non-alternant hydrocarbons without ASC.



Γ_n

Reprint requests to Professor Ivan Gutman.

0932-0784 / 94 / 1100-1053 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

In this paper we find an explicit expression for the determinant of the adjacency matrix of n-circulene. If n is even then by means of (1) we immediately obtain the respective algebraic structure count. For the sake of completeness we also deduce a similar expression for the Kekulé structure count. All these quantities are expressed in terms of Fibonacci numbers.

The k-th Fibonacci number F_k is defined by means of the recurrence relation $F_k = F_{k-1} + F_{k-2}$ and by means of the initial conditions $F_0 = F_1 = 1$. Some properties of Fibonacci numbers, that are needed in the subsequent considerations, are deduced in the Appendix.

We note in passing that some of our results could have been expressed in a more compact form in terms of Lucas numbers L_k which are defined as $L_k = F_k + F_{k-2}$. We nevertheless prefer the somewhat better known Fibonacci numbers.

The Determinant of the Adjacency Matrix of Γ_n

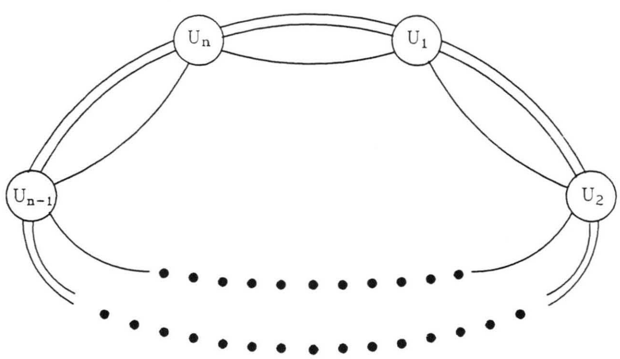
Let G denote a graph possessing N vertices and let $A(G)$ be its adjacency matrix. The characteristic polynomial of G is denoted by $\phi(G, x)$ and is defined as

$$\phi(G, x) = \det[x I_N - A(G)]$$

where I_N is the unit matrix of order N. Evidently,

$$\det A(G) = (-1)^N \phi(G, 0) . \quad (2)$$

Now, let G be a rotagraph [16–18], i.e., a graph with the following structure:



The fragments $U_1, U_2, \ldots, U_n$ are isomorphic. Further, the way how a fragment U_j is connected to its left neighbor (U_{j-1}) and its right neighbor (U_{j+1}) is same for all $j = 1, 2, \ldots, n$, assuming that $U_{n+1} \equiv U_1$ and $U_0 \equiv U_n$

The characteristic polynomial of a rotagraph is factorized as [16, 17]

$$\phi(G, x) = \prod_{j=1}^{n} \det\left[x I_{N/n} - A(U) - \omega_j J_L(U) - \omega_j^* J_R(U)\right], \quad (3)$$

where $\omega_j = \exp(2ij\pi/n)$, $\omega_j^* = \exp(-2ij\pi/n)$ and $i = \sqrt{-1}$. In (3) $A(U)$ is the adjacent matrix of any of the fragments U_j, whereas $J_L(U)$ and $J_R(U)$ describe the connections between U_j and its left and right neighbor, respectively.

Formula (3) has its origin in solid state quantum physics (see, for example, [19, 20]). It belongs to the standard tools of chemical graph theory; for some of its most recent applications see [21, 22].

The molecular graphs of circulenes are rotagraphs; their fragments U_j have four vertices each. Consequently, by means of (3) the characteristic polynomial of Γ_n is factored into n quartic polynomials:

$$\phi(\Gamma_n, x) = \prod_{j=1}^{n} P_j(x) ,$$

where

$$P_j(x) = \det\begin{bmatrix} x-\omega_j-\omega_j^* & -1 & 0 & 0 \\ -1 & x & -1 & -\omega_j \\ 0 & -1 & x & -1 \\ 0 & -\omega_j^* & -1 & x \end{bmatrix} .$$

Direct calculation yields

$$P_j(x) = \left(x - 2\cos(2j\pi/n)\right)\left(x^3 - 3x - 2\cos(2j\pi/n)\right) - (x^2 - 1) .$$

Bearing (2) in mind, we see that

$$\det A(\Gamma_n) = \prod_{j=1}^{n} \left[1 + \left(2\cos(2j\pi/n)\right)^2\right] . \quad (4)$$

Formula (4) can be viewed as just a routine result, obtained by utilizing the existence of an n-fold symmetry axis in Γ_n. We now prove another, less straightforward property of $\det A(\Gamma_n)$.

Theorem 1: If F_k is the k-th Fibonacci number, then

$$\det A(\Gamma_n) = \begin{cases} 25\,(F_{n/2-1})^4 & \text{if } n \text{ is even,} \\ 5\,(F_{n-1})^2 & \text{if } n \text{ is odd.} \end{cases} \quad (5)$$

Proof: Let C_n be the circuit with n vertices (= the molecular graph of the n-annulene). A well known result in both theoretical chemistry [23] and graph spectral theory [24] is that the eigenvalues of C_n are

$2\cos(2j\pi/n)$, $j = 1, 2, \ldots, n$. Bearing this in mind, the right-hand side of (4) can be rewritten as

$$\prod_{j=1}^{n} \left[1 + \left(2\cos(2j\pi/n)\right)^2\right]$$
$$= \prod_{j=1}^{n} \left(i - 2\cos(2j\pi/n)\right) \prod_{j=1}^{n} \left(-i - 2\cos(2j\pi/n)\right)$$
$$= \phi(C_n, i)\, \phi(C_n, -i)\,. \tag{6}$$

The characteristic and the matching polynomials of the circuit C_n are related as [25]

$$\phi(C_n, x) = \alpha(C_n, x) - 2\,, \tag{7}$$

whereas the matching polynomial of C_n obeys the recursion relation [26]

$$\alpha(C_n, x) = x\,\alpha(C_{n-1}, x) - \alpha(C_{n-2}, x)\,. \tag{8}$$

The first few polynomials $\alpha(C_n, x)$ are: (9)

$$\alpha(C_1, x) = x;\ \alpha(C_2, x) = x^2 - 2;\ \alpha(C_3, x) = x^3 - 3x;$$
$$\alpha(C_4, x) = x^4 - 4x^2 + 2;\quad \alpha(C_5, x) = x^5 - 5x^3 + 5x\,.$$

From (8) we readily obtain a Fibonacci-type recursion formula

$$[(\mp i)^n\, \alpha(C_n, \pm i)] \tag{10}$$
$$= [(\mp i)^{n-1}\, \alpha(C_{n-1}, \pm i)] + [(\mp i)^{n-2}\, \alpha(C_{n-2}, \pm i)]\,.$$

Taking into account (9), it is easy to verify that the solution of (10) reads

$$(\mp i)^n\, \alpha(C_n, \pm i) = F_n + F_{n-2}\,.$$

Combining this result with (7) we conclude that

$$\phi(C_n, \pm i) = (\pm i)^n\, (F_n + F_{n-2}) - 2\,,$$

by means of which the right-hand side of (6) can be expressed in terms of Fibonacci numbers. Direct calculation yields

$$\prod_{j=1}^{n} \left[1 + \left(2\cos(2j\pi/n)\right)^2\right]$$
$$= \begin{cases} [F_n + F_{n-2} - (-1)^{n/2}\, 2]^2 & \text{if } n \text{ is even,} \\ (F_n + F_{n-2})^2 + 4 & \text{if } n \text{ is odd}\,. \end{cases} \tag{11}$$

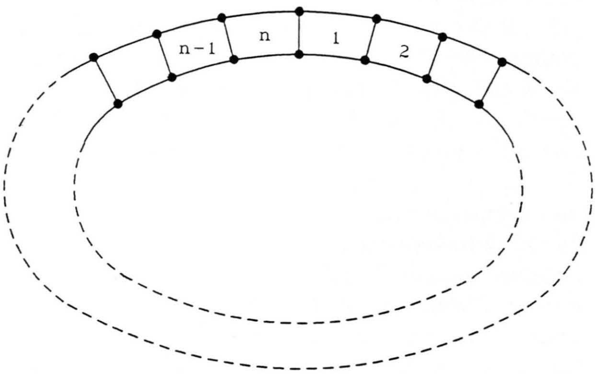
Because the left-hand side of (6) is just the determinant of the adjacency matrix of the molecular graph of n-circulene, for even values of n, Theorem 1 follows from (11) and the identity (A 5) deduced in the Appendix. For odd values of n Theorem 1 follows from (11) and the identity (A 7). □

Combining (1) and (5) we see that the algebraic structure count of n-circulene is given by (12), that, of course, holds only for even n:

$$\mathrm{ASC}\{\Gamma_n\} = 5\,(F_{n/2-1})^2\,. \tag{12}$$

The Number of Kekulé Structures of Γ_n

The number of Kekulé structures of the n-circulene will be denoted by $K\{\Gamma_n\}$. This quantity is precisely the same as the number of perfect matchings of the cyclic ladder graph CL_n of length n.



$\mathrm{CL_n}$

To see this, recall that if the graph G' is obtained from a graph G by inserting two new vertices (of degree two) to an arbitrary edge of G, then G' and G have equal numbers of perfect matchings [22]. The cyclic ladder graph was recently studied by Hosoya and Harary [22], and the number of its perfect matching was shown to be equal to $F_n + F_{n-2} + 1 + (-1)^n$. Consequently,

$$K\{\Gamma_n\} = F_n + F_{n-2} + 1 + (-1)^n\,. \tag{13}$$

Note that the result expressed in (13) is essentially the same as what Bergan et al. [27] obtained for the Kekulé structure count of primitive coronoids with angularly annelated hexagons.

Using the identities (A 5) and (A 8) given in the Appendix, we arrive at

$$K\{\Gamma_n\} = \begin{cases} (F_{n/2} + F_{n/2-2})^2 & \text{if } n \equiv 0 \pmod 4, \\ 5\,(F_{n/2-1})^5 & \text{if } n \equiv 2 \pmod 4, \\ F_n + F_{n-2} & \text{if } n \text{ is odd}\,. \end{cases} \tag{14}$$

Combining (12) and (14) and bearing in mind the identity (A 7), the following relations between the

ASC- and K-values of (even) circulenes are obtained:

$$\mathrm{ASC}\{\Gamma_n\} = K\{\Gamma_n\} - 4 \quad \text{if} \quad n \equiv 0 \pmod 4, \tag{15a}$$

$$\mathrm{ASC}\{\Gamma_n\} = K\{\Gamma_n\} \quad \text{if} \quad n \equiv 2 \pmod 4. \tag{15b}$$

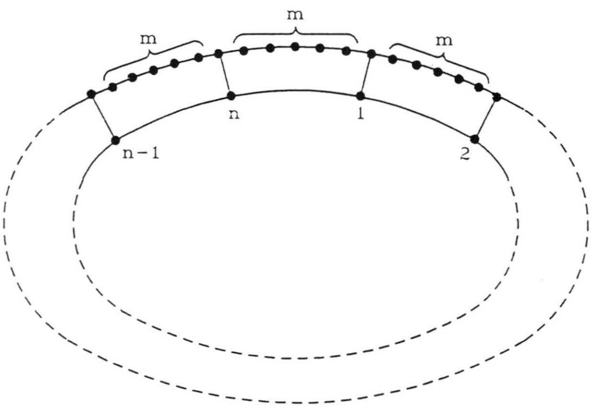
In addition to this, we have

$$\det A(\Gamma_n) = (K\{\Gamma_n\})^2 + 4 \quad \text{if } n \text{ is odd}.$$

Equation (15b) reveals the (not too surprising) fact that all the Kekulé structures of $(4k+2)$-circulenes are of the same parity. From (15a) we see that in $4k$-circulenes all but two Kekulé structures are of the same parity. Hence, there is only a small "correction" [12, 13] that has to be made to the Kekulé structure counts of $4k$-circulenes and no correction whatever in the case of $(4k+2)$-circulenes. This would imply the conclusion that there is no significant difference between the π-electron conjugation and aromaticity of $4k$- and $(4k+2)$-circulenes. The same applies to odd and even circulenes. (Topological consideration fails to take into account steric effects. Therefore the conclusions based on the analysis of the Kekulé structures only should be interpreted with appropriate caution. Different sizes of the inner perimeter may cause drastic steric strain and non-planarity in circulenes, distorting the π-electron network beyond the applicability of the simple Kekulé-structure-based theoretical models.)

A Generalization: Circulenes with Ring Sizes Different from Six

In this section we compute the determinants of the adjacency matrices of the graphs $\Gamma_{n,m}$ that are obvious generalizations of the molecular graphs of circulenes.



$\Gamma_{n,m}$

Evidently, $\Gamma_{n,m}$ coincides with the circulene graph if $m = 2$, and is equal to the cyclic ladder if $m = 0$.

We first recall a long-known result [28]: If the graph G' is obtained from a graph G by inserting four new vertices (of degree two) to an arbitrary edge of G, then the determinants of the adjacency matrices of G' and G are equal. Its immediate consequence is the following:

Theorem 2: If $m \equiv m' \pmod 4$, then

$$\det A(\Gamma_{n,m}) = \det A(\Gamma_{n,m'}).$$

In view of Theorem 2, the problem of the computation of $\det A(\Gamma_{n,m})$ is reduced to the finding of the determinants of the adjacency matrices of $\Gamma_{n,0}$, $\Gamma_{n,1}$, $\Gamma_{n,2}$ and $\Gamma_{n,3}$. The case of $\Gamma_{n,2}$ has already been solved (Theorem 1). Employing a symmetry-factoring method analogous to what was used to obtain (4), we arrive at

Theorem 3: If $m \equiv 2 \pmod 4$, then $\det A(\Gamma_{n,m})$ is equal to the right-hand side of (5). In addition to this,

(a) if $m \equiv 0 \pmod 4$, then

$$\det A(\Gamma_{n,m}) = \begin{cases} 0 & \text{if } n \equiv 0 \text{ or } n \equiv 3 \pmod 6, \\ 3 & \text{if } n \equiv 1 \text{ or } n \equiv 5 \pmod 6, \\ 9 & \text{if } n \equiv 2 \text{ or } n \equiv 4 \pmod 6; \end{cases}$$

(b) if $m \equiv 1 \pmod 4$, then

$$\det A(\Gamma_{n,m}) = \begin{cases} 0 & \text{if } n \text{ is even}, \\ 8 & \text{if } n \text{ is odd}; \end{cases}$$

(c) if $m \equiv 3 \pmod 4$, then

$$\det A(\Gamma_{n,m}) = 0 \quad \text{for all values of } n.$$

Observe that the formula given under (a) embraces also the case of the cyclic ladders.

The most remarkable feature of Theorem 3 is that the forms of the expressions for $\det A(\Gamma_{n,m})$, $m \equiv 0, 1, 3 \pmod 4$ are completely different from the respective expression for $m \equiv 2 \pmod 4$. Whereas $\det A(\Gamma_{n,2})$ is found to be a function of the n-th or $(n/2)$-th Fibonacci number and thus exponentially increases with increasing n, the other three determinants assume only a limited number of values (one, two or three) and exhibit a certain periodicity when regarded as functions of n. Theorems 1 and 3 imply that the circulene graphs have distinguished graph-spectral properties, particularly when compared with the similarly structured graphs $\Gamma_{n,m}$.

For completeness we mention that for even values of m, the number of perfect matchings (= Kekulé structure count) of $\Gamma_{n,m}$ is the same as of Γ_n, (13) and (14). On the other hand, for odd values of m

$$K\{\Gamma_{n,m}\} = \begin{cases} 4 & \text{if } n \text{ is even}, \\ 0 & \text{if } n \text{ is odd}. \end{cases}$$

Appendix. Some identities for Fibonacci numbers

Lemma 1: For $a, b \geq 1$,

$$F_{a+b} = F_a F_b + F_{a-1} F_{b-1} . \tag{A 1}$$

Proof proceeds by induction on the number b. □

For $a = b$, formula (A 1) reduces to

$$F_{2a} = (F_a)^2 + (F_{a-1})^2 . \tag{A 2}$$

Lemma 2: For $a, b \geq 1$ and $0 \leq t \leq \min\{a, b\} - 1$,

$$F_{a+1} F_{b-1} - F_a F_b = (-1)^t [F_{a+1-t} F_{b-1-t} - F_{a-t} F_{b-t}] . \tag{A 3}$$

Proof: Using the facts that $F_{a+1} = F_a + F_{a-1}$ and $F_b = F_{b-1} + F_{b-2}$, we transform the left-hand side of (A 3) into $F_{a-1} F_{b-1} - F_a F_{b-2}$ which is exactly the right-hand side of (A 3) for $t = 1$. Repeating this procedure t times we arrive at (A 3). □

Choosing $a = b = p - 1$ and $t = p - 2$ we have the following special case of (A 3):

$$F_p F_{p-2} - F_{p-1} F_{p-1} = (-1)^p . \tag{A 4}$$

Lemma 3: For $p \geq 1$,

$$F_{2p} + F_{2p-2} - (-1)^p\, 2 = 5\,(F_{p-1})^2 . \tag{A 5}$$

Proof: Using (A 2), the left-hand side of (A 5) is transformed as

$$\begin{aligned} & F_{2p} + F_{2p-2} - (-1)^p\, 2 \\ &= [(F_p)^2 + (F_{p-1})^2] + [(F_{p-1})^2 + (F_{p-2})^2] - (-1)^p\, 2 \\ &= 4(F_{p-1})^2 + [(F_p)^2 + (F_{p-2})^2 - 2 F_p F_{p-2}] + 2 F_p F_{p-2} \\ &\quad - 2 F_{p-1} F_{p-1} - (-1)^p\, 2 . \end{aligned} \tag{A 6}$$

Because of (A 4),

$$2 F_p F_{p-2} - 2 F_{p-1} F_{p-1} - (-1)^p\, 2 = 0 ,$$

and therefore (A 6) becomes

$$F_{2p} + F_{2p-2} - (-1)^p\, 2 = 4(F_{p-1})^2 + [F_p - F_{p-2}]^2 .$$

Lemma 3 follows now from the obvious relation $F_p - F_{p-2} = F_{p-1}$. □

Lemma 4: For $n \geq 2$,

$$(F_n + F_{n-2})^2 = 5\,(F_{n-1})^2 + (-1)^n\, 4 . \tag{A 7}$$

Proof: Use the evident identity

$$\begin{aligned} (F_n + F_{n-2})^2 &= (F_n - F_{n-2})^2 + 4 F_n F_{n-2} \\ &= (F_n - F_{n-2})^2 + 4\,(F_{n-1})^2 + 4(F_n F_{n-2} - F_{n-1} F_{n-1}) , \end{aligned}$$

combine it with (A 4) and take into account $F_n - F_{n-2} = F_{n-1}$. □

By (A 5) and (A 7) we have the following corollary to Lemmata 3 and 4:

Corollary. For $p \geq 1$,

$$F_{2p} + F_{2p-2} + (-1)^p\, 2 = (F_p + F_{p-2})^2 . \tag{A 8}$$

Acknowledgements

One of the authors (I.G.) thanks the Mathematical Institute in Belgrade for financial support.

[1] S. J. Cyvin and I. Gutman, Kekulé Structures in Benzenoid Hydrocarbons, Springer-Verlag, Berlin 1988.
[2] I. Gutman and S. J. Cyvin, Introduction to the Theory of Benzenoid Hydrocarbons, Springer-Verlag, Berlin 1989.
[3] I. Gutman and S. J. Cyvin (eds.), Advances in the Theory of Benzenoid Hydrocarbons (Topics in Current Chemistry 153), Springer-Verlag, Berlin 1990.
[4] S. J. Cyvin, J. Brunvoll, and B. N. Cyvin, Theory of Coronoid Hydrocarbons, Springer-Verlag, Berlin 1991.
[5] I. Gutman (ed.), Advances in the Theory of Benzenoid Hydrocarbons II (Topics in Current Chemistry 162), Springer-Verlag, Berlin 1992.
[6] W. E. Barth and R. G. Lawton, J. Amer. Chem. Soc. **88,** 380 (1966); **93,** 1730 (1971).
[7] K. Yamamoto, T. Harada, M. Nakazaki, T. Naka, Y. Kai, S. Harada, and N. Kasai, J. Amer. Chem. Soc. **105,** 7171 (1983).
[8] B. Thulin and O. Wennerström, Acta Chem. Scand. **B 30,** 369 (1976).
[9] M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Roy. Soc. London **A 214,** 482 (1952).
[10] C. F. Wilcox, Tetrahedron Lett. **1968,** 795.
[11] A. Graovac, I. Gutman, and N. Trinajstić, Topological Approach to the Chemistry of Conjugated Molecules, Springer-Verlag, Berlin 1977.

[12] W. C. Herndon, Tetrahedron **29,** 3 (1973).
[13] W. C. Herndon, J. Chem. Educ. **51,** 10 (1974).
[14] I. Gutman and N. Trinajstić, Croat. Chem. Acta **47,** 35 (1975).
[15] I. Gutman, M. Randić, and N. Trinajstić, Rev. Roum. Chim. **23,** 383 (1978).
[16] O. E. Polansky and N. N. Tyutyulkov, Commun. Math. Chem. **3,** 149 (1977).
[17] A. Graovac and D. Babić, Z. Naturforsch. **40a,** 66 (1985).
[18] D. Babić, A. Graovac, B. Mohar, and T. Pisanski, Discr. Appl. Math. **15,** 731 (1986).
[19] P. W. Anderson, Concepts in Solids, Benjamin, Reading 1971.
[20] G. G. Hall, Molecular Solid State Physics, Springer-Verlag, Berlin 1991.
[21] G. G. Hall, Internat. J. Quantum Chem. **45,** 167 (1993).
[22] H. Hosoya and F. Harary, J. Math. Chem. **12,** 211 (1993).
[23] C. A. Coulson and A. Streitwieser, Dictionary of π-Electron Calculations, Freeman, San Francisco 1965.
[24] D. Cvetković, M. Doob, and H. Sachs, Spectra of Graphs – Theory and Application, Academic Press, New York 1980, p. 53.
[25] H. Hosoya, Theor. Chim. Acta **25,** 215 (1972).
[26] I. Gutman and H. Hosoya, Theor. Chim. Acta **48,** 279 (1978).
[27] J. L. Bergan, B. N. Cyvin, and S. J. Cyvin, Acta Chim. Hung. **124,** 299 (1987); see also [2], p. 128.
[28] I. Gutman and N. Trinajstić, Croat. Chem. Acta **45,** 423 (1973).