

Permanental Polynomials of the Smaller Fullerenes

Gordon G. Cash*

New Chemicals Screening and Assessment Branch, Risk Assessment Division (7403), Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, 1200 Pennsylvania Avenue, N.W., Washington, DC 20460

Received March 31, 2000

Using a general computer code developed previously, permanental polynomials were computed for all fullerenes $C_{\leq 36}$. Mathematical properties of the coefficients and zeroes were investigated. For a given isomer series of constant n , the $n/2$ independent zeroes appear to consist of a set of 10 that are nearly constant within the series and a set of $n/2 - 10$ that differ greatly with structure.

INTRODUCTION

Previous work described an algorithm for computing the permanental polynomial of a chemical graph.¹ The present paper discusses the properties of this polynomial for the fullerenes up through C_{36} relative to those of the more extensively studied characteristic (secular) and acyclic (matching) polynomials. The coefficients and zeroes of all the polynomials are available as Supporting Information. As used here, the term *fullerene* has its most common meaning as a spheroidal, all-carbon cage with only pentagonal and hexagonal faces and all vertices of degree 3.

The primary purpose of this study was to demonstrate practical application of the permanental polynomial algorithm described previously. The smaller fullerene structures were selected for two reasons. The possible fullerene structures have been generated and catalogued.²

Moreover, a very large number of theoretical papers concerning these structures has been published, so opportunities would exist to look for correlations between parameters calculated from the permanental polynomials and those calculated in other ways.³

METHODS

Calculations were conducted on PC-compatible computers with CPU clock speeds of 133–233 MHz and 32 or 64 Mb of RAM. Coefficients of the permanental polynomials were calculated with code written by the author and described previously. Factors and zeroes were determined with Mathematica using the built-in Factor[] and NSolve[] functions. The Mathematica documentation⁴ noted that the Factor[] function is known to be imperfect.

RESULTS

Coefficients. The following discussion uses the convention normally used for numbering the coefficients of characteristic polynomials, namely, the index of the coefficient increases as the exponent decreases, so that for a graph with n vertices, the polynomial is

$$\sum_{i=0}^n a_i x^{n-i}$$

As explained previously,¹ for fullerenes, the terms $a_i x^{n-i}$ of the permanental polynomial have $a_i \geq 0$ for all even i and $a_i \leq 0$ for odd i . Even alternants have all $a_i = 0$ for odd i , but nonalternants such as fullerenes have $a_i < 0$ for most odd i .

The value of the largest positive coefficient of the permanental polynomial, a_{\max} , is closely related to the size of the structure. There is, however, some variation within an isomer series. For example the largest a_{\max} for a C_{36} fullerene is 536 053 704, and the smallest is 521 053 930; the numbers differ from each other by <3%. The average values of a_{\max} , however, for C_{20-36} fit the equation $\ln(a_{\max}) = 0.5808n - 0.8478$, $r = 0.999985$. For the systems studied, the maximum coefficient is always associated with the same power of x . However, there seems to be no compelling reason for believing that this should be strictly true for all systems, and even in the smaller systems, there are cases where the largest and second-largest coefficients are within about 2% of each other. The average values of the C_{36} permanents themselves, a_n , provide nearly as good a fit: $\ln(a_n) = 3.217n - 3.204$, $r = 0.999941$. There is also somewhat more variation among the a_0 , the smallest (192 528) being only 91.5% of the largest (210 425).

It has long been known that a_n gives the Kekulé count (K) for alternant structures⁵ but not for nonalternants such as fullerenes. However, Cash demonstrated a correlation between $\ln a_0 / \ln K$ and certain structural features of fullerenes.⁶ Possible uses of the other coefficients of the permanental polynomial remain to be investigated. Many uses have been made of the zeroes of the characteristic polynomials of chemical graphs (commonly called the spectra of the graphs).⁷ Now that efficient methods exist for computing the coefficients of the acyclic, or matching, polynomial,⁸⁻¹⁰ more uses for those coefficients are beginning to appear in the literature.¹¹ These findings suggest that the future may see a similar variety of uses for the permanental polynomial coefficients.

Zeroes. As noted in the previous paper,¹ the zeroes of permanental polynomials of fullerenes are all complex. Since

* Corresponding author phone: (202)260-3900; fax: (202)260-1236; e-mail: cash.gordon@epa.gov.

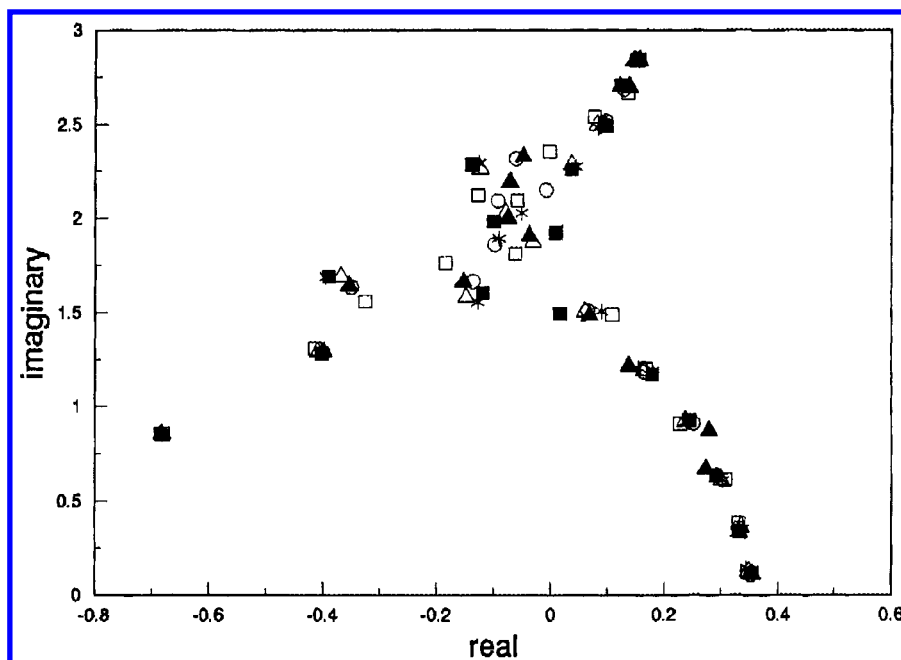


Figure 1. The zeroes of the permenental polynomials of the six C_{34} fullerene isomers plotted in the complex plane. For each point shown, there is another with the same real value but with imaginary value of opposite sign. The scale of the real axis has been expanded relative to the imaginary to facilitate visualization. Clusters with the seven lowest (<1.3) and three highest (>2.4) values on the imaginary axis are seen to have much less scatter than the other seven clusters. All isomer series studied possess this feature, although the limiting values are not necessarily the same.

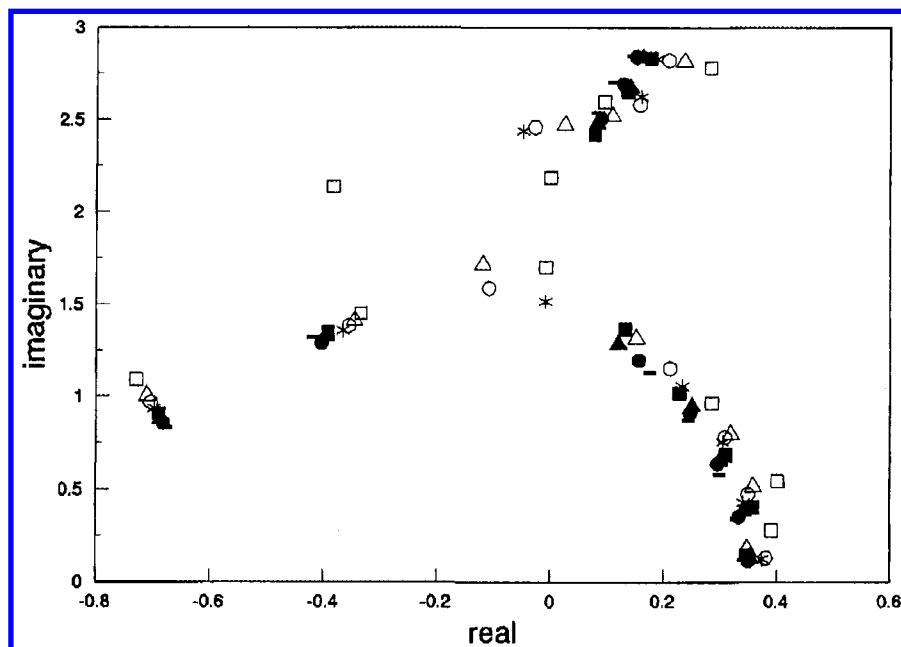


Figure 2. Average values of the zeroes of the permenental polynomial for each isomer series plotted in the complex plane: C_{20} (\square), C_{24} (\triangle), C_{26} (\circ), C_{28} ($*$), C_{30} (\blacksquare), C_{32} (\blacktriangle), C_{34} (\bullet), C_{36} ($-$). Several obvious progressions in carbon-number order are apparent. Also, C_{20} is readily seen to be the most different from the others. The points near the edges of the plot are tightly clustered, while those near the center are most varied.

the polynomial for C_n is of degree n , there are $n/2$ such pairs of zeroes. Note that the permenental polynomial of a fullerene cannot have a root $\lambda = 0$ because then the permanent, which is the product of all the roots, would be zero. This cannot be the case because the permanent is always at least as large as the Kekulé structure count K ,⁵ and Klein and Liu proved¹² that $K \geq 3$ for all fullerene cages.

Recently, Aihara et al.¹³ computed zeroes for both characteristic and matching polynomials for all fullerenes up through C_{70} . Their comparisons across isomer series

showed that, for characteristic polynomials, the zeroes for molecules of the same size are very different, while for matching polynomials, the zeroes for different isomers are nearly identical. Perhaps the most important finding in the present work is that the permenental polynomial provides a situation intermediate between these two. Of the $n/2$ independent zeroes, ten are nearly constant across an isomer series, while the remaining $n/2 - 10$ vary greatly with structure. Figure 1 shows the results for the six isomers of C_{34} fullerene. Looking at average values (and for C_{34} ,

individual values as well), the ten zeroes that characterize an isomer series are always those with the three largest and seven smallest values on the imaginary axis. Indeed, for all the fullerenes up through C_{36} , there is only one instance in which a pair of individual values fails to meet this criterion. (For one of the C_{2v} isomers of C_{30} , the zero $0.0911 + 2.3675i$ belongs to the set of ten, while $-0.0885 + 2.3852i$ does not.) The scatter is of course not apparent with C_{20} , which has only ten independent zeroes, nor with C_{24} and C_{26} , which have only one isomer each. It is not yet known whether any quantitative relationships exist between the scattered points and structural or physicochemical properties of the fullerenes from which they are derived.

The ten zeroes that seem to characterize any given isomer series also vary in a systematic way with molecular size. Figure 2 is a plot of average values of the ten zeroes for each isomer series C_{20-36} . (C_{20} , C_{24} , and C_{26} are the "averages" of single points, and C_{22} does not exist.) Several of the clusters in Figure 2 are nearly straight lines. The best is the cluster near $-0.7 + 0.9i$ (most negative on the real axis), which gives the linear regression equation $y = -4.99x - 2.55$, $n = 8$, $r = 0.998$. The cluster near $0.2 + 2.8i$ (most positive on the imaginary axis) gives $y = 0.432x + 2.91$, $n = 8$, $r = 0.977$. Finally, the cluster near $-0.4 + 1.3i$ gives $y = 1.57x + 1.95$, $n = 8$, $r = 0.929$. In all three cases, the order of points on the line is the order of increasing (or decreasing) carbon number. It seems very likely that these correlations are real and not simply fortuitous, but their meaning is far from clear. Many uses have been made of the zeroes of the characteristic polynomials of chemical graphs.⁷ As with the coefficients, this may suggest future uses for the permanental polynomial zeroes as well.

CONCLUSIONS

A newly described method for generating all coefficients of the permanental polynomial of an adjacency matrix was applied to the fullerenes up through C_{36} . The zeroes of these polynomials showed unexpected patterns. Of the independent zeroes, ten are nearly constant within an isomer series, while the remaining zeroes vary greatly with structure. Average values for the ten zeroes that characterize an isomer series change in a systematic way with increasing carbon number. This suggests that the permanental polynomial encodes a

variety of structural information. Much future work remains to be done in elucidating the extent to which this polynomial encodes structural features in a quantitative way as well as in exploring the relationship of the polynomial to structure in systems other than fullerenes.

ACKNOWLEDGMENT

This document has been reviewed by the Office of Pollution Prevention and Toxics, USEPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

Supporting Information Available: Coefficients of the permanental polynomials of the fullerenes C_{20} through C_{36} (Table 1) and the zeroes of those polynomials (Table 2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- (1) Cash G. G. The Permanental Polynomial. *J. Chem. Inf. Comput. Sci.* **2000**, 40, 1203–1206.
- (2) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes*; Clarendon Press: Oxford, 1995.
- (3) For example: Cioslowski, J. *Electronic Structure Calculations on Fullerenes and Their Derivatives*; Oxford University Press: New York, 1995; Chapter 7, and references therein.
- (4) Wolfram, S. *Mathematica: A System for Doing Mathematics by Computer*, 2nd ed.; Addison-Wesley: Reading, MA, 1991; p 609.
- (5) Cvetković, D.; Gutman, I.; Trinajstić, N. Kekulé Structures and Topology. *Chem. Phys. Lett.* **1972**, 16, 614–616.
- (6) Cash, G. G. Permanents of Adjacency Matrices of Fullerenes. *Polycycl. Arom. Comput.* **1997**, 12, 61–69.
- (7) Trinajstić, N. *Chemical Graph Theory*, 2nd ed.; CRC Press: Boca Raton, FL, 1992; Chapter 5.
- (8) Babić, D.; Brinkmann, G.; Dress, A. Topological Resonance Energy of Fullerenes. *J. Chem. Inf. Comput. Sci.* **1997**, 37, 920–923.
- (9) Salvador, J. M.; Hernandez, A.; Beltran, A.; Duran, R.; Mactutis, A. Fast Partial-Differential Synthesis of the Matching Polynomial of C_{72-100} . *J. Chem. Inf. Comput. Sci.* **1998**, 38, 1105–1110.
- (10) Cash, G. G.; Herndon, W. C. Novel Approaches to Exact Coefficients of Acyclic Polynomials. *MATCH* **1999**, 40, 273–278.
- (11) See, for example: Dias, J. R. Resonance Structures of Benzenoid Conjugated Radicals. *Phys. Chem. Chem. Phys.* **1999**, 1, 5081–5086.
- (12) Klein, D. J.; Liu, X. Theorems for Carbon Cages. *J. Math. Chem.* **1992**, 11, 199–205.
- (13) Aihara, J.; Babić, D.; Gutman, I. Matching spectra of fullerenes. *MATCH* **1996**, 33, 7–16.

CI0000326