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Strongly Subspectral Series Containing the Cyclobutadiene Moiety

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Series of strongly subspectral molecular graphs (having a preponderance of common eigenvalues) corresponding to conjugated hydrocarbon polyenes containing cyclobutadiene moieties are presented and their electronic/structural properties studied.

Key words: molecular graphs, conjugated polyenes, cyclobutadiene

INTRODUCTION

Our goal is to understand the properties of molecules by identifying elementary substructures that are carriers of this information in compact form. Examples of elementary substructures (subgraphs) are atoms (graph vertices), bonds (graph edges or lines), rings (graph circuits),[1] excised internal structures (subgraphs spanned by the internal vertices),[2] elementary aufbau units (C_4H_2, C_3H, and C_2),[3] elementary capping units (C_6, C_5, C_2, C, and edge),[4] organic functional groups (subgraphs with a collection of weighted edges and vertices), monomeric units (repeating subgraphs), 1-factor, 2-factor, and Sachs subgraphs, Ulam subgraphs,[1] embedding fragments (Hall subgraphs),[5] and right-hand mirror-plane fragments (McClelland subgraphs).[6,7] Excised internal structures and elementary aufbau units are important in the enumeration of polycyclic conjugated hydrocarbons, and elementary capping units are important in the generation of fullerene structures. 1-Factor, 2-factor, Sachs, Ulam, Hall, and McClelland subgraphs have found application in the determination of eigenvalues (energy levels) and

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eigenvectors (wave functions) of molecular graphs (vertex-line depictions corresponding to C-C σ-bond skeletons of conjugated hydrocarbons). Molecular graphs having one or more eigenvalues in common are called subspectral. If they have a preponderance of eigenvalues in common, they are said to be *strongly* subspectral. An important method for identifying subspectral molecular graphs is the method of Hall which he called embedding.[5] Details for the procedure of embedding can be found in several sources.[5,7] For example, if a smaller molecular graph can be embedded on a larger one, then the smaller one is a Hall subgraph of the larger one establishing that the latter must have eigenvalues common to the former.[5,7]

Repetitive attachment of given aufbau units under prescribed rules can lead to families (series) of molecular graphs exhibiting characteristic trends. This is the essence of the aufbau principle. If the smaller members of these families correspond to known molecules, then one can use these trends to predict the properties of larger unknown members. Molecules with strongly subspectral molecular graphs are more similar. Beginning with a pair of strongly subspectral molecular graphs, successive attachment of the same aufbau unit under certain conditions can lead to a pair of series having a one-to-one correspondence between member molecules of each generation. This approach allows one to systematically study progressive changes in properties among a large number of related molecules that would be difficult to accomplish by other methods.

PAIRS OF INFINITE STRONGLY SUBSPECTRAL SERIES

Figures 1–5 present five sets of series containing molecular graph members that are pairwise strongly subspectral for each successive generation. Similarly, Figure 6 presents three series that are strongly subspectral. The first molecular graph in the series in Figures 1–4 and 6 are zero generation members and the eigenvalues affixed next to each are unique to the whole series; the zero generation pair of molecular graphs can be disconnected and are not necessarily be strongly subspectral. The zero generation molecular graphs are frequently Hall subgraphs[5–7] for every member of the respective series. The eigenvalues common to each pair of molecular graphs are listed below the respective members. The formula of the aufbau unit is indicated in the upper left-hand corner of each figure. Although, the smaller corresponding members of a strongly subspectral series can look quite different, as their size increases they begin to look more similar and in the infinite limit become *virtually* identical.

The pairs of infinite series tabulated in Figures 1 and 2 have the same Hall subgraphs, ethene and allyl, and all these series devolve to the same infinite limit member. Ethene and 3-methylene-1,4-pentadiene (first genera-

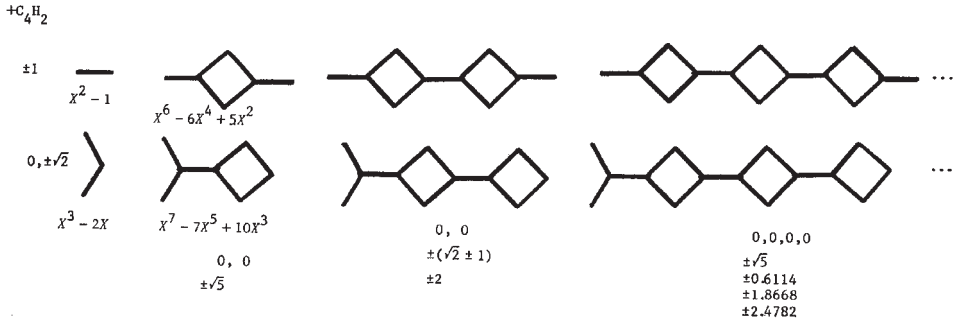

Figure 1. Two series of molecular graphs that are strongly subspectral. The unmatched eigenvalues are indicated next to the zero generation molecular graphs of ethene and allyl. Using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursion $P_n(X) = (X^4 - 5X^2)P_{n-1}(X) - 4X^2P_{n-2}(X)$.

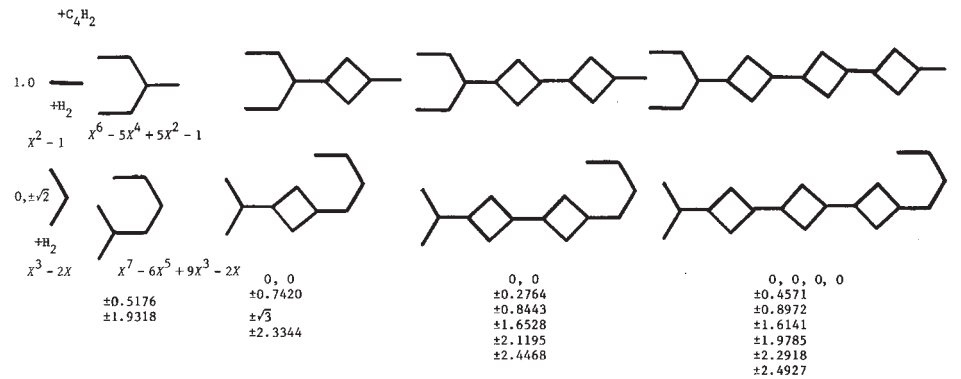

Figure 2. Two series of strongly subspectral molecular graphs. The unmatched eigenvalues are indicated next to the zero generation members of each series. Using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursion $P_n(X) = (X^4 - 5X^2)P_{n-1}(X) - 4X^2P_{n-2}(X)$.

tion member in the top series of Figure 2) are known molecular species, and allyl is a well-known reactive intermediate. 1,3-Dimethylenecyclobutadiene (2^{nd} molecular graph in the upper series of Figure 1) is a diradical isomer of benzene that has been photolytically generated and studied in a low temperature glassy matrix of 2-methyltetrahydrofuran.[8] Ethene and allyl are zero generation members of the series in Figures 1–2. All the remaining molecular graphs in Figures 1 and 2 correspond to unknown molecules. The characteristic and matching polynomials for the members in the second

(lower) series in Figure 1 have been studied by Hosoya.[9] Allyl is also among the the zero generation members of the infinite series contained in Figures 3, 4 and 6. Cyclobutadiene (Figures 3 and 4) is a transient intermediate.[10,11] The trimethylenemethane, tetramethyleneethane, *m*-xylylene (2^{nd} molecular graph in the middle row of Figure 6), and cyclobutadiene diradicals and molecules corresponding to the first generation molecular graphs in Figure 1 have been experimentally and theoretically studied.[12–14] Both 3-methylene-1,4-pentadiene (Figure 2) and styrene (Figure 5) are reactive liquids

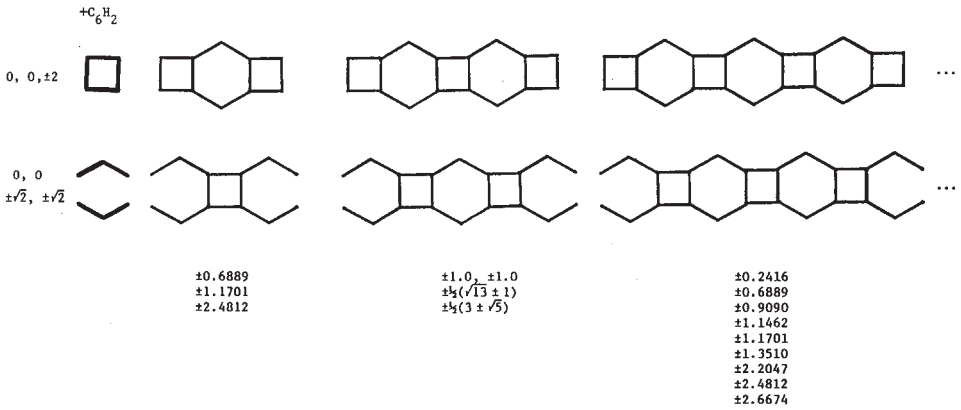

Figure 3. Two series of molecular graphs that are strongly subspectral. The unmatched eigenvalues are indicated next to the zero generation member of each series.

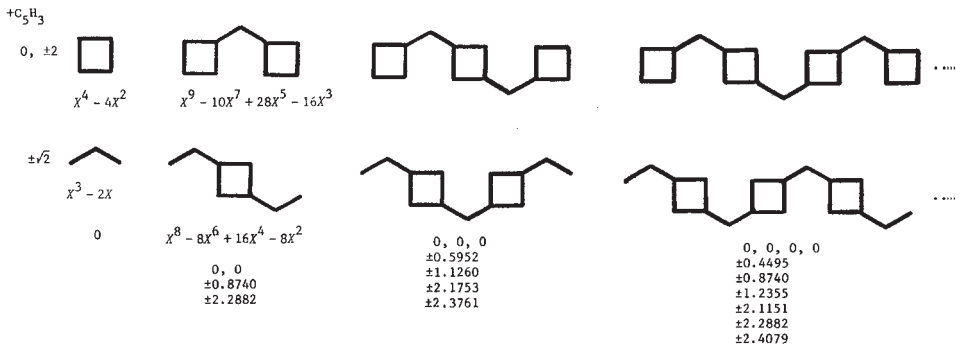

Figure 4. Two series of molecular graphs that are strongly subspectral. The unmatched eigenvalues are indicated next to the zero generation molecular graphs (cyclobutadiene and allyl). Using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursion $P_n(X) = (X^5–6X^3+4X)P_{n–1}(X)–4X^2P_{n–2}(X)$.

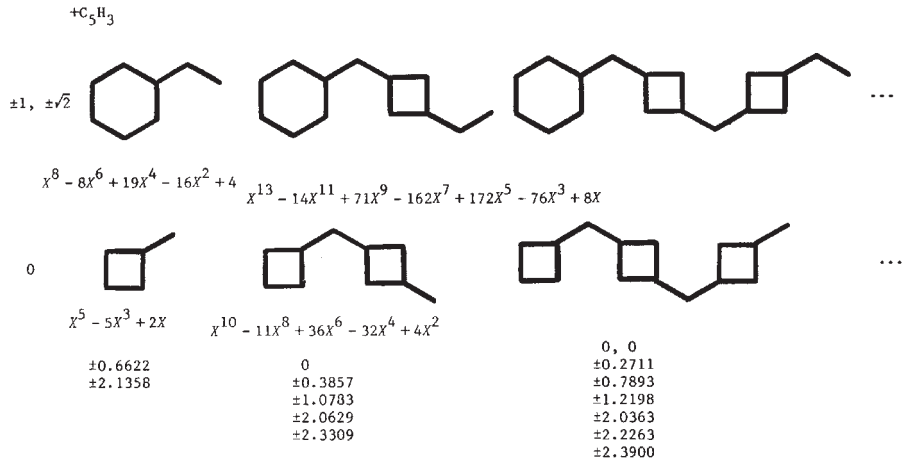

Figure 5. Two series of molecular graphs that are strongly subspectral. The unmatched eigenvalues are indicated to the left of the first generation member of each series. Using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursion $P_n(X) = (X^5–6X^3+4X)P_{n–1}(X)–4X^2P_{n–2}(X)$.

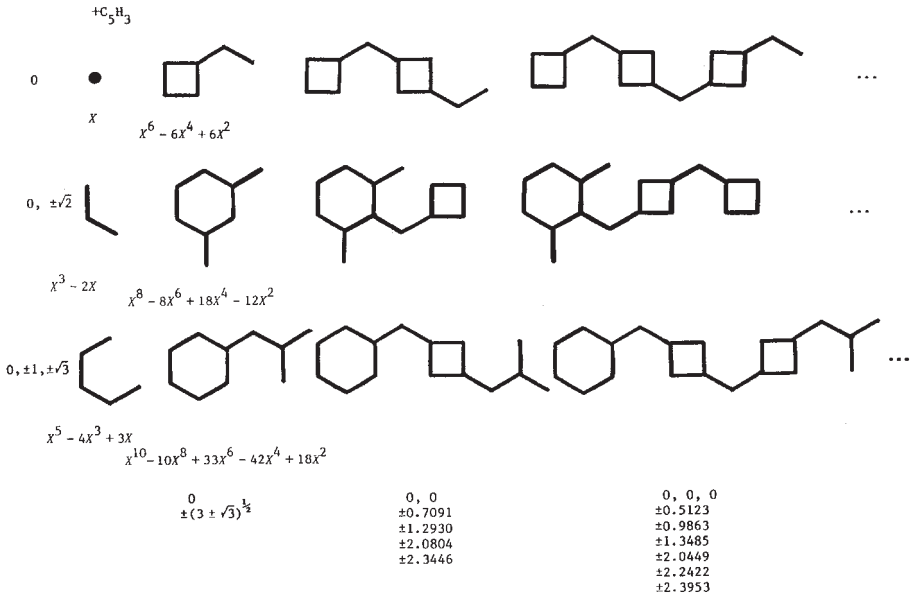

Figure 6. Three series of molecular graphs that are strongly subspectral. The unmatched eigenvalues are indicated to the left of the first molecular graphs (zero generation member) of each series. Using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursion $P_n(X) = (X^5–6X^3+4X)P_{n–1}(X)–4X^2P_{n–2}(X)$.

that readily polymerize. Thus, almost all the zero and first generation molecular graphs in Figures 1–6 correspond to known moderate to very reactive molecules.

The aufbau unit for any strongly subspectral pair of series will be either identical but connected differently or strongly subspectral with the same number of vertices. The aufbau unit is the same for all four series in Figures 1–2 and may be either cyclobutadiene-1,3-diyl or trimethylenemethanetetrayl; with the former aufbau unit successive generation of the members of these series will involve a splicing-in operation. 3,4-Dimethylenecyclobutenetetrayl is the aufbau unit for the series in Figure 3, and methylenecyclobutadienediyl is the aufbau unit for the series in Figures 4–6.

DIMETHYLENEPOLYCYCLOBUTADIENE AND RELATED INFINITE SERIES

The molecular graphs in the upper series of Figure 1 correspond to the dimethyelenepolycyclobutadiene series studied theoretically.[13] Each member of this series is isomeric to a benzenoid acene with the same number of rings. All the molecular graphs in the upper series can be embedded by ethene, and all molecular graphs in the lower series can be embedded by allyl, *i.e.,* ethene is a Hall subgraph to all members of the upper series and allyl is a Hall subgraph to all members of the lower series. The first generation molecular graph (2^{nd} molecular graph) can be embedded on the third, fifth, seventh, *etc.* generation molecular graphs, the second generation molecular graph can be embedded on the fifth, eighth, *etc*., and so forth. Everything mentioned for the upper series on embedding applies to the lower series.

The two NBMOs in trimethylenemethane diradical have atoms in common whereas the two NBMOs of tetramethyleneethane diradical are confined to different sets of atoms. The NBMOs in the former are said to be nondisjoint and in the latter disjoint.[14] Thus, the two NBMOs trimethylenemethane are degenerate, singly occupied MOs which are orthogonal but coextensive; exchange interaction in coextensive systems favors the high-spin (triplet) state. The first generation member in the upper series of Figure 1, 1,3-dimethylenecyclobutadiene diradical, has two nondisjoint NBMOs and the second generation member, dimethylenedicyclobutadiene, has two disjoint NBMOs. In general, theory predicts that when the number of cyclobutadiene rings in dimethylenpolycyclobutadiene is odd, the corresponding molecule should have a triplet ground state, and when the number of rings is even, a singlet ground state.[13,14] In the infinite limit, the singlet and triplet states will be degenerate.

The infinite limit members of the pair of strongly subspectral series in Figure 1 have the same density of states and, as we will see, a zero bandgap. A zero bandgap of an infinite strip is equivalent to a HOMO-LUMO energy difference of zero for a smaller molecule which does not possess a continuum energy levels, and the molecular graphs (except the zero generation members) in Figures 1–2 and 4–6 have HOMO-LUMO = 0 values of increasing degeneracy as their size increase. The overlapping close proximity of energy levels (continuum) in infinitely large π-electronic networks result in bands bounded by singularities, where the continuum of occupied energy levels is called the valence band, and the continuum of unoccupied energy levels above the valence band is called the conduction band. If there is a zone containing no energy levels between the valence and conduction bands, then this zone is referred to as a bandgap. Electrical conductivity in a polymer network is associated with a zero bandgap.

Hosoya and coworkers[15] have shown that the singular points to the density of states of a periodic polymer is given by the eigenvalues of the hypothetical cyclic dimer (sometimes cyclic monomer) having the same recurring aufbau unit (unit cell); if this cyclic dimer has NBMOs, then the corresponding periodic polymer has a zero HOMO-LUMO bandgap or isolated NBMOs between the valence and conduction bands.[9,15] To illustrate, consider the infinite linear polycyclobutadiene strip which we argue is the limit species to the series in both Figures 1–2. The general expression for the infinite polymer ring having the same repetitive (aufbau) unit as polycyclobutadiene is

$$X^4 - 5X^2 - 4X\cos\theta_k = 0$$

$$\theta_k = 2k\pi/n \text{ for } k = 0, 1, 2, \ldots, n-1.$$

Solution of this equation for the cyclic dimer ($n = 2$) gives eigenvalues 0, 0, ± 1, $\pm \frac{1}{2}(\sqrt{13} \pm 1)$ which correspond to the singularities for the density of states. Factoring out X from the above equation and setting $X = 0$ in the remaining factor gives $\cos\theta_k = 0$. Thus, the infinite polycyclobutadiene polymer has a zero bandgap and is expected to possibly form conductive materials.

BENZODICYCLOBUTADIENE AND RELATED INFINITE SERIES

Two strongly subspectral infinite series are presented in Figure 3. The first generation member (2^{nd} molecular graph) of the upper series in Figure 3 is benzodicyclobutadiene; only one persubstituted derivative of benzodicyclobutadiene has been prepared.[16] In the upper series of Figures 3–4, cyclobutadiene can be embedded on every member of these series, and in the

lower series, allyl can be embedded on every other member. In upper series of Figure 3, benzodicyclobutadiene can be embedded on the third, fifth, seventh, *etc*. generation members, the second generation molecular graph can be embedded on the fifth, eighth, *etc*., and so forth. This process of progressive embedding of smaller members of an infinite series on larger members can be used to iteratively generate the density of states of the infinite limit member. Also, this iterative process suggests that the eigenvalues of the smaller molecular graphs should have the higher degeneracy in the limit member of a infinite series.

Using Hosoya's method,[9,15] the density of states for the infinite limit member to the series in Figure 3 has been determined to be given by the general expression of

$$X^6 - 8X^4 - 4X^3\cos\theta_k + 12X^2 + 8X\cos\theta_k + 4\cos^2\theta_k - 4 = 0$$

which gives eigenvalues of $0, 0, \pm\sqrt{2}, \pm\sqrt{2}, \pm(1 \pm \sqrt{3}), \pm 2$ for the boundaries of the density of states and a zero bandgap. Thus, polybenzocyclobutadiene is expected to be conductive.

The pair of strongly subspectral series in Figure 4 can be derived from those in Figure 3 by a vertex deletion procedure. For example, deleting a vertex from position-3 of benzodicyclobutadiene (the first generation member in the upper series of Figure 3) gives the first generation molecular graph in the upper series of Figure 4, and deleting the four vertices in the plane of tetravinylcyclobutadiene (the first generation member in the lower series of Figure 3) gives the first generation molecular graph in the lower series. Using Hosoya's method,[9,15] the density of states for the infinite limit member to the series in Figures 4–6 has been determined to be given by the general expression of

$$X^5 - 6X^3 + 4X(1 - \cos\theta_k) = 0$$

which gives eigenvalues of $0, 0, 0, 0, \pm\sqrt{2}, \pm 2.0, \pm 2.4495$ for the boundaries of the density of states and a zero bandgap.

RECURSION RELATIONS FOR POLYMERS WITH SINGLY CONNECTED MONOMERIC UNITS

All the series in Figures 1–2 devolve to the same infinite limit π-electronic system and have the same following recursion relation

$$P_n(X) = (X^4 - 5X^2)P_{n-1}(X) - 4X^2P_{n-2}(X)$$

where n = 0, 1, 2, 3, ... corresponds to the generation number. Note that $P_0(X) = X^2 - 1$ for the upper series in Figures 1–2 and $P_0(X) = X^3 - 2X$ in the two lower series. $P_1(X)$ differs for all four series in Figures 1–2. The coefficients of $(X^4 - 5X^2)$ and $4X^2$ are determined by the characteristic polynomial of the C_4H_2 aufbau unit (cyclobutadienediyl). The characteristic polynomial for the cyclobutadiene monomer is $X^4 - 4X^2$. Since another bond is formed for each attachment of this monomer to the polymer chain and 4 corresponds to the number of edges (bonds) in the C_4 molecular graph, this second coefficient must be incremented by one to give $X^4 - 5X^2$ as the characteristic polynomial for the aufbau unit.

The recursion relation for the series in Figures 4–6 is given by

$$P_n(X) = (X^5 - 6X^3 + 4X)P_{n-1}(X) - 4X^2P_{n-2}(X)$$

where C_5H_3, methylenecyclobutadienediyl, is the aufbau unit. The characteristic polynomial for methylenecyclobutadiene is $X^5 - 5X^3 + 2X$. Since another bond is formed for each attachment of this monomer to the polymer chain and 5 corresponds to the number of edges (bonds) in the corresponding molecular graph, this second coefficient must be incremented by one and the third coefficient [$a_4 = \frac{1}{2}(q^2 - 9q + 6N_c) - 2r^4 = 4$] (Ref. 7) must also be amended since it is a function of the number of molecular graph edges (q). Thus, the characteristic polynomial for the methylenecyclobutadienediyl aufbau unit is $X^5 - 6X^3 + 4X$.

The $4X^2$ coefficient arises from the way these aufbau units are connected which is basically the same for the two different aufbau units for the series in Figures 1–2 and 4–6. An alternative way to acquire these aufbau characteristic polynomials is by setting $\cos\theta_k = 0$ in the corresponding prior cyclic dimer expressions. Techniques for finding recursion relations for these type of polymers have been discussed by Hosoya.[9]

DESIGN OF STRONGLY SUBSPECTRAL SERIES

While the discovery of strongly subspectral series is mainly empirical, some general guiding rules can be summarized. Starting with two empirically found strongly subspectral molecular graphs, search for an aufbau unit in which different attachments leads to two successor molecular graphs that are also strongly subspectral. In this search, keep in mind that successive attachments should eventually result in extended systems that begin to look more and more alike, and the dettachment of this aufbau will frequently give zero generation molecular graph members possessing the unique eigenvalues. The zero generation molecular graphs are often embedding fragments for every member of the respective series.

SUMMARY

The design of NBMO degenerate systems continues to attract the interest of investigators[17] and the aufbau principle in generating strongly subspectal series is another approach. Subspectrality is one measure of molecular similarity and the aufbau principle can lead to infinite pairs of series whose membership is pairwise strongly subspectral. This provides a strategy for predicting the properties of unknown molecules from known ones if they both have membership to such a pair of series. This paper presents new results that further extends our previous work.[18]

The results of Figures 1–6 suggest that end groups have a greater influence on smaller polymer chains than larger ones. The three different infinite polymer strips containing the cyclobutadiene moiety have zero bandgaps and are expected to be conductive materials.

Coupling Hosoya's method of using cyclic boundary conditions in the analysis of infinite linear polymers with our concept of strongly subspectral series allows us to not only determine the precise end points for the density of states but also gives us a another perspective. The simultaneous study of a large group of molecules as herein done would be prohibitively time consuming using *ab initio* methods, whereas, this approach allows easy discovery of analytical expressions and trends in large groups of related molecules.

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SAŽETAK

Jako subspektralna serija molekularnih grafova koji sadrže ciklobutadien

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Proučavana je skupina jako subspektralnih molekulskih grafova, pretežito sa zajedničkim svojstvenim vrijednostima. Ti grafovi predstavljaju konjugirane poliene koji sadrže ciklobutadien. Pretkazana su njihova strukturna i elektronska svojstva.