

## On subspectral problem—benzenoid hydrocarbons with common eigenvalues $\pm 1$

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**Summary.** The method for the contraction and expansion of graphs is used to treat the subspectrality of benzenoid hydrocarbons in relation to eigenvalues  $\pm 1$ . Counts of benzenoid hydrocarbons together with degeneracies of eigenvalues have been carried out for all species having  $h \leq 7$  hexagons. In addition, twelve homologous series are evaluated, and the closed results for the distribution of eigenvalues  $\pm 1$  and degeneracies in terms of the number of repeated units are tabulated. This method is universal and applicable to cases sharing other eigenvalues and to nonbenzenoid systems.

**Key words:** Benzenoid hydrocarbon — Hückel theory — Graph spectrum — Subspectrality

### 1. Introduction

The phenomenon of different molecules sharing one or several eigenvalues in the Hückel framework has intrigued chemists for many years. Most works concern the factorization of the characteristic polynomial (CP) by means of symmetry analysis [1–6], which yields incomplete information on the subspectrality of molecules [7, 11]. Others have used the Heilbronner procedure [1] to show why the eigenvalues of a fragment sometimes appear in the spectrum of the larger composite molecule [7–10]. In a series of papers, Hall [11] provided the basis for recognition of the eigenvalues  $\pm 1$  and  $\pm 2$  for alternant hydrocarbons; his rule was translated into a descriptive form called embedding. Dias [12] commented on the method of embedding and pointed out that embedding seems to be a

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sufficient but not a necessary requirement for the presence of a set of eigenvalues. He developed the "selective lineation" method of identifying  $\pm 1$  eigenvalues for dealing effectively with some periferused benzenoid hydrocarbons. Nevertheless, it is desirable to be able to find subspectral molecules in general and to enumerate all molecular graphs with the specified structural feature of one or more shared eigenvalues.

In a previous paper [13], the graph-contracting method was used to generate and enumerate the concealed non-Kekulean benzenoid hydrocarbons. This method is also effective in discussing the subspectral problem in relation to eigenvalues  $\pm 1$ . In this paper, we give an account of our treatment, illustrating the enumeration of all such species having seven and less hexagons in accordance with the degeneracy of eigenvalues  $\pm 1$ . Moreover, twelve homologous series of benzenoid hydrocarbons are evaluated and a set of closed results for the distribution of eigenvalues  $\pm 1$  and degeneracies dependent on the number of repeated units are tabulated. This gives an insight into how a regularity in the density of states varies in finite and infinite systems without the assumed cyclic boundary condition.

## 2. Mathematical background

As is well known, the characteristic polynomial (CP) of graph  $G$  is defined as follows

$$P_G(X) = \det |xI - A| \quad (1)$$

where  $I$  is the identity matrix and  $x$  is a variable. The adjacency matrix  $A$  in Eq. (1) is typically sparse with entries in the  $i$ th row and  $j$ th column:

$$a_{ij} = \begin{cases} 1 & \text{if vertices } i \text{ and } j \text{ are connected,} \\ 0 & \text{otherwise.} \end{cases} \quad (2)$$

Thus, when dealing with CPs, it would be convenient to use a weighted graph in which each vertex is subject to the weight  $x$  and the edge keeps the standard value 1. Usually, a loop is introduced to specify the vertex with weight not equal to 0. However, it seems too laborious to draw all loops in a big graph; therefore we omit them completely, but specifically symbolize those vertices and edges having weight other than  $x$  and 1 respectively. In the later discussions, we take  $x$  (or  $x = \pm 1$ ) as the standard weight of vertex unless otherwise specified.

The following theorem is of fundamental importance [14].

**Theorem 1.** *Let the graph  $G$  be partitioned into two sub-graphs  $A$  and  $B$  by erasing edges. Then we have*

$$P_G(x) = P_B(x)P_{A'}(x) \quad (3)$$

where  $A'$  is a modified version of  $A$ , obtained by adjusting the weight of vertices and edges in  $A$  that were originally connected with  $B$  in the following manner.

(1) If vertex  $i$  in  $A$  is the end of erased edges  $ij$  ( $j = 1, 2, \dots, t$ ) and there

are  $r$  circuits ( $c = c_1, c_2, \dots, c_r$ ) shared by vertex  $i$  and different paths ( $p = c_1 - i, c_2 - i, \dots, c_r - i$ ) in  $B$ , then the weight of vertex  $i$  should be adjusted to

$$y_i = x - [P_B(x)]^{-1} \left[ \sum_{j=1}^i a_{ij}^2 P_{B-j}(x) + 2 \sum_{c=c_1}^{c_r} \pi_c P_{B-(c-i)}(x) \right] \quad (4)$$

where  $\pi_c$  is equal to the product of edge weights along the circuit  $c$ .

(2) If vertices  $i$  and  $k$  in  $A$  are ends of erased edges  $ij$  and  $kl$  respectively and there are  $s$  paths ( $p = p_1, p_2, \dots, p_s$ ) connecting vertices  $j$  and  $l$  in  $B$ , then the weight of edge  $ik$  is equal to

$$b_{ik} = a_{ik} + \sum_{j,l} \sum_{p=p_1}^{p_s} a_{ij} a_{kl} \pi_p P_{B-p}(x) / P_B(x) \quad (5)$$

where  $\pi_p$  represents the product of edge weights along the path  $p$ .

In practice, it is easy to write down these modified weights because factors  $\pi_c, a_{ij} a_{kl} \pi_p$  are always equal to 1, and the summations in Eqs. (4) and (5) are limited to a few terms. For an illustration, consider the benzene graph partitioned according to the two different schemes shown in Fig. 1. In scheme 1,  $A'$  is ethene like with weight  $y$  and  $b$  for the identical vertices and edge, respectively, which are equal to

$$y = x - g_3(x)/g_4(x), \quad b = 1 + 1/g_4(x) \quad (6)$$

according to Eqs. (4) and (5). Similarly in scheme 2,  $A'$  is a single vertex with weight  $z$  calculated from Eq. (4):

$$z = x - 2[g_4(4) + 1]/g_5(x). \quad (7)$$

On substituting them into Eq. (3), both lead to

$$P_G(x) = g_6(x) - g_4(x) - 2. \quad (8)$$

In Eqs. (6)–(8),  $g_n(x)$  represents the CP of a linear chain with  $n$  vertices, namely

$$g_n(x) = \sum_{r=0}^{[n/2]} (-1)^r (n-r)! / r!(n-2r)! x^{n-2r}. \quad (9)$$

When  $x = 1$  (or  $-1$ ), the situation becomes even simpler because Eq. (9) is reduced to

$$g_n(1) = (-1)^m (\delta_{n,3m} + \delta_{n,3m+1}) \quad (m = 0, 1, 2, \dots) \quad (10)$$

where  $\delta_{a,b}$  is the Kronecker symbol; more specifically,  $g_n(1) = 0$ , if  $n = 2, 5, 8, \dots$ ,  $g_n(1) = 1$ , if  $n = 0, 1, 6, 7, \dots$  and  $g_n(1) = -1$  for  $n = 3, 4, 9, 10, \dots$ . Thus when  $x = 1$ , we have  $y = 0$  and  $b = 0$  for benzene graph, implying that  $A'$  is composed of two isolated vertices with zero weight and

$$P_G(1) = g_4(1)0^2 = 0^2. \quad (11)$$

Therefore, benzene contains eigenvalues  $\pm 1$  with double degeneracies. This result is better exhibited in Fig. 2.

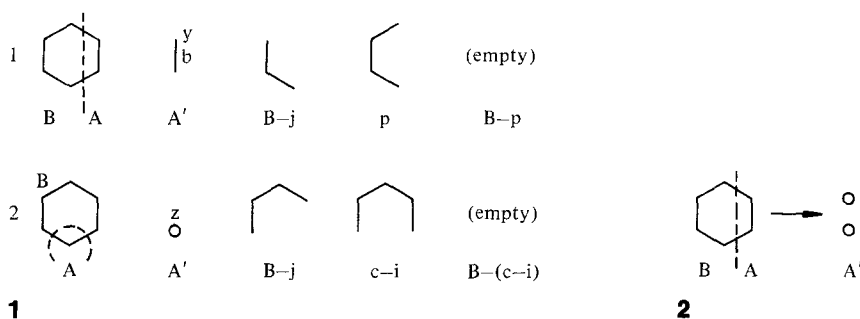


Fig. 1. Two schemes for partitioning the benzene graph. Symbols are those used in Eqs. (4) and (5)

Fig. 2. Contraction of benzene graph for testing the existence of eigenvalue 1. The *open circles* signify vertices with zero weight

### 3. Detection and construction of subspectral molecules

The role played by Eq. (3) in determining the subspectrality of molecules is quite obvious. Because  $P_B(x)$  appears in Eqs. (4) and (5) as a denominator, it can not be equal to zero; therefore the necessary and sufficient condition for  $x$  to be the eigenvalue of  $G$ , namely  $P_G(x) = 0$  is

$$P_{A'}(x) = 0. \quad (12)$$

Thus, by selecting the fragment  $B$  appropriately, we can make  $A'$  so simple that Eq. (12) can be proved readily. In the case that the molecular graph  $G$  is rather complicated, the fragment  $B$  would be multi-component, namely a series of smaller fragments  $B_1, B_2, \dots, B_m$  are selected in order to make the modified graph  $A'$  as simple as possible. They satisfy

$$P_G(x) = P_{B_1}(x)P_{B_2}(x) \cdots P_{B_m}(x)P_{A'}(x) \quad (13)$$

and the subspectrality relationship between molecular graphs  $G$  and  $A'$  can then be determined from Eq. (12). On the other hand, a small graph with eigenvalue  $x$  is able to couple with a fragment or a set of fragments in the way fulfilling Eq. (13) such that a big molecular graph is generated, involving the same eigenvalue  $x$ . This means that the forward direction of Eq. (3) or Eq. (13) exhibiting the contraction of graph  $G$  is suitable for the detection of individual eigenvalues, and the opposite direction displaying the expansion of a graph with inherent eigenvalue  $x$  can be used to construct subspectral molecules of various sizes.

The situation looks more meaningful when  $A'$  coincides with  $A$ , namely  $A' = A$ , because  $G$  then shares the eigenvalue  $x$  with its fragment  $A$ . In the case that  $x$  is not an eigenvalue of  $G$ , the condition  $A' = A$  implies the equivalence of  $G$  and  $A$  which can be arranged to give a composite species  $G[A]G'$  subspectral to  $G'$ , where  $G[A]G'$  is produced by coalescing  $G$  and  $G'$  with the shared fragment  $A$ . We shall formulate this principle into corollaries later. Also, we limit attention to the plus eigenvalue  $+1$  with no loss of generality, since benzenoid hydrocarbons are alternant.

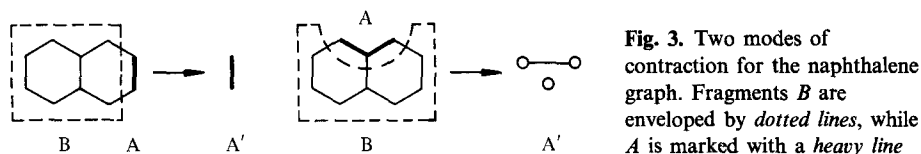


Fig. 3. Two modes of contraction for the naphthalene graph. Fragments  $B$  are enveloped by dotted lines, while  $A$  is marked with a heavy line

We have shown why benzene contains double eigenvalues 1 as exhibited in Fig. 2 or Eq. (11). Now, we consider naphthalene. Two different modes of contraction are displayed for comparison as shown in Fig. 3. In the first contraction, we have  $B = 5,6$ -dimethylenecyclohexadiene with  $P_B(1) = -1$  and  $A' = A =$  ethene with  $P_{A'}(1) = 0$ ; for the second contraction,  $P_B(1) = g_7(1) = 1$  and  $A'$  is bi-component, with a zero weight vertex and an ethene-like fragment with zero weight vertices. From Eq. (3), these two modes of contraction give

$$P_G(1) = (-1)0 = 0, \quad P_G(1) = 1(-1)0 = 0, \quad (14)$$

respectively, implying that naphthalene is singly degenerate in eigenvalues  $\pm 1$ .

The condition  $A' = A =$  ethene inspires one to coalesce naphthalene with other species  $G'$  by a shared edge (depicted by the heavy line in the first mode of Fig. 3) without changing the inherent eigenvalues of  $\pm 1$  in  $G'$ . Thus anthracene is found to have  $\pm 1$  eigenvalues with double degeneracy similar to benzene, whereas naphacene and 1,2-benzanthracene (see Fig. 4) are singly degenerate in  $\pm 1$  eigenvalues. By induction, the argument can be generalized to show that polyacenes of  $N$  hexagons (Fig. 4) share eigenvalues  $\pm 1$  with degeneracies 1 for even  $N$  and 2 for odd  $N$ . This result was discussed by Hall, based on an analysis of the symmetry of the eigenvectors [11].

Next we consider phenalenium, a perifused species with three hexagons, for which we perform the contraction indicated in Fig. 5. This gives  $P_B(1) = 1$  and  $P_{A'}(1) = 0^3$  so that

$$P_G(1) = P_B(1)P_{A'}(1) = (1)0^3 \quad (15)$$

for phenalenium. Hence phenalenium is triply degenerate in eigenvalues  $\pm 1$ .

The reverse of the transformations shown in Figs. 2, 3 and 5 display the formation of benzene, naphthalene and phenalenium from appropriate smaller fragments  $A'$  and  $B$  respectively. They are also available for producing other species sharing  $\pm 1$  eigenvalues with definite degeneracy. In Fig. 6, graph  $A'_1$  can be contracted into benzene graph on the one hand, and extended to a perifused species  $G_1$  by coupling with a butadiene fragment (see Fig. 2) on the other. Thus, molecule  $G_1$  is known to have  $\pm 1$  eigenvalues with double degeneracy similar to benzene.

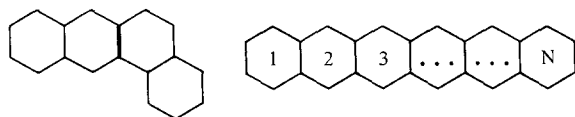
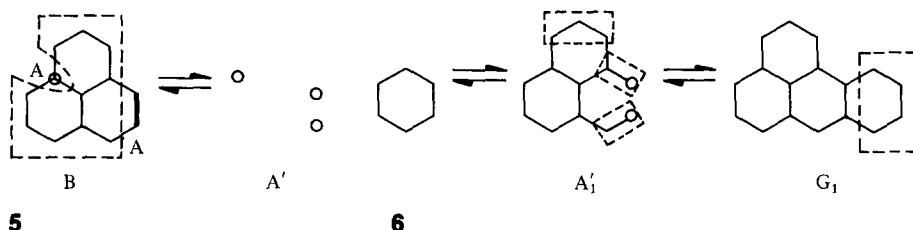


Fig. 4. 1,2-benzanthracene and polyacene graphs



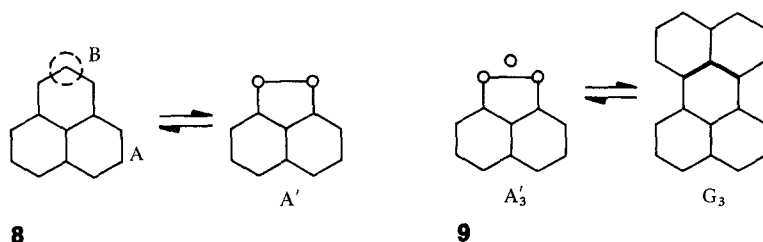
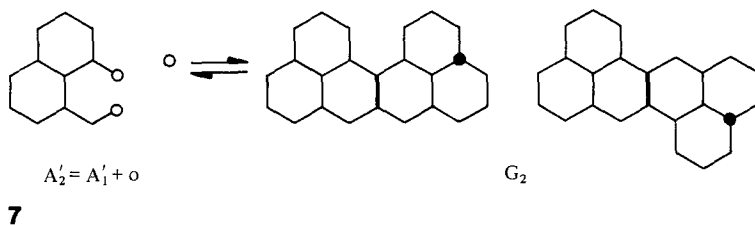
**Fig. 5.** Contraction of phenalenium when  $x = 1$ .  $A$  is a bi-component, consisting of a vertex and an ethene fragment (denoted by the heavy line)

**Fig. 6.** Generation of perifused graph  $G_1$ ; open circles in  $A'_1$  represent vertices with zero weight

The contraction of phenalenium inspires one to realise that  $A'_2$ , a bi-component graph composed of  $A'_1$  (Fig. 6) and a zero weight vertex, can be extended into two perifused species without changing the three inherent pairs of  $\pm 1$  eigenvalues (see Fig. 7).

Phenalenium can also be partitioned as depicted in Fig. 8. In this case  $A'$ , an acenaphthenylene like graph with two zero weight vertices, invariably has three pairs of  $\pm 1$  eigenvalues in accord with Eq. (3). The perylene graph, which has an extra pair of eigenvalues  $\pm 1$ , may then be produced by analogy with the result for the second mode of contraction of naphthalene (see Fig. 3); this is shown in Fig. 9.

The contraction presented in Fig. 9 can be used to find almost all benzenoid hydrocarbons sharing eigenvalues  $\pm 1$ .



**Fig. 7.** Two perifused benzenoid hydrocarbons sharing eigenvalues  $\pm 1$  with triple degeneracy. The heavy edge and vertex in  $G_2$  will be reduced to three open circles in  $A'$  on carrying out the contraction displayed in Fig. 5

**Fig. 8.** An equivalent version of phenalenium having three pairs of  $\pm 1$  eigenvalues

**Fig. 9.** Generation of the perylene graph; the allyl fragment in  $G_3$  will be reduced to open circles in  $A'_3$  on carrying out the second mode of contraction displayed in Fig. 3

#### 4. Searching out subspectral species having $h \leq 7$ hexagons

In order to construct subspectral benzenoids sharing  $\pm 1$  eigenvalues conveniently by means of Theorem 1, it is worthwhile formulating certain corollaries related to the condition that  $A' = A$ .

**Corollary 1.** *Let  $G$  be one of the acyclic fragments shown in Fig. 10 where the heavily marked vertex is elected as  $A$ . Then the weight of vertex of  $A$  does not change if its connecting fragment  $B$  is deleted.*

This is quite in accordance with Eq. (4).

**Corollary 2.** *The fragment  $B = 5,6$ -dimethylenecyclohexadiene can be deleted terminally from benzenoids without any influence on the occurrence of  $\pm 1$  eigenvalues in the remaining part  $A$ .*

This has been illustrated in the first mode of contraction of naphthalene, where  $A$  is an ethene fragment (see Fig. 3).

Additional results can be obtained by joining Corollary 2 with Corollary 1, namely deleting 5,6-dimethylenecyclohexadiene and allyl fragments in succession without modifying  $A$ . In Fig. 11, three kinds of molecular graphs are displayed in which heavy lines identify  $A$ , the equivalent fragment of  $G$  when  $x = 1$ .

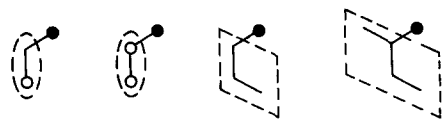


Fig. 10. Acyclic fragments  $B$  (enveloped with dotted line) can be deleted without changing the connected vertex,  $A$

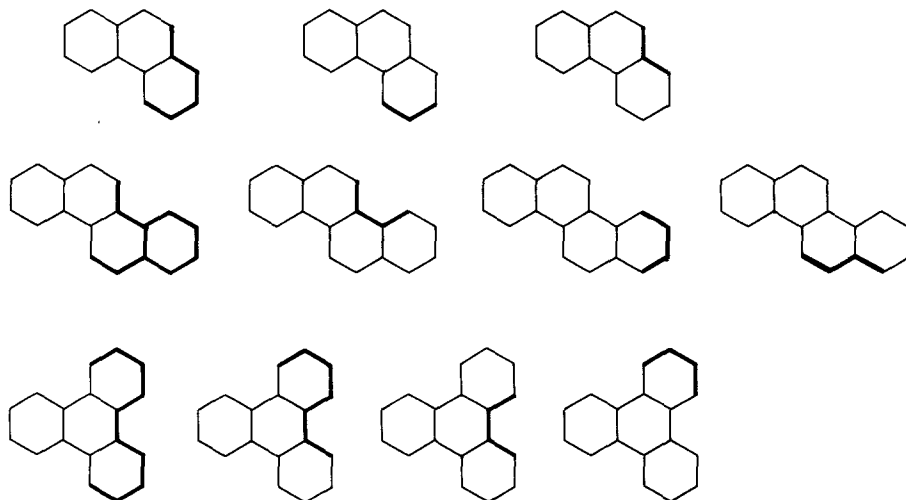


Fig. 11. Equivalent fragments (heavy lines) of phenanthrene, Chrysene and triphenylene graphs

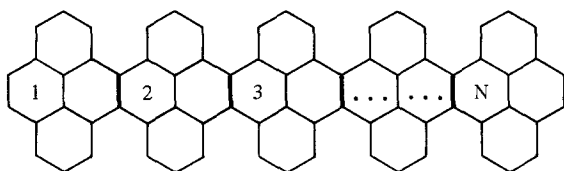


Fig. 12. Homologous series with a single pair of  $\pm 1$  eigenvalues

**Corollary 3.** *The fragment  $B = \text{phenanthrene}$  can be deleted from pyrene graph leaving  $A$ , the ethene fragment, unchanged. This can be verified analogously, using Eqs. (4) and (5). By induction, the polymer displayed in Fig. 12 can easily be shown to have a single pair of eigenvalues  $\pm 1$  independent of the length  $N$ .*

**Corollary 4.** *Molecular graph  $G'$  having eigenvalues  $\pm 1$  can be coalesced with another graph  $G$  by sharing the equivalent fragment  $A$  of  $G$  such that the composite species  $G[A]G'$  shares eigenvalues  $\pm 1$  with degeneracy identical to  $G'$ .*

This was suggested earlier and illustrated by polyacene in Fig. 4 as well as the polymer in Fig. 12.

In order to obtain benzenoid hydrocarbons sharing eigenvalues  $\pm 1$ , elementary subspectral species together with degeneracies are displayed in Fig. 13. They play a role in generating various composite species  $G[A]G'$  subspectral to  $G'$ .

The benzenoid hydrocarbons of less than four hexagons that share eigenvalues  $\pm 1$  are benzene, naphthalene, anthracene and phenallene. We have also found four species with four hexagons sharing eigenvalues  $\pm 1$ ; three of these have already been displayed in Figs. 4, 6 and 12. By means of Corollary 4, the final 4-hexagonal species, benzo[*c*]phenanthrene, is derived as the composite graph  $G[A]G'$  with a pair of eigenvalues  $\pm 1$  shown in Fig. 14.

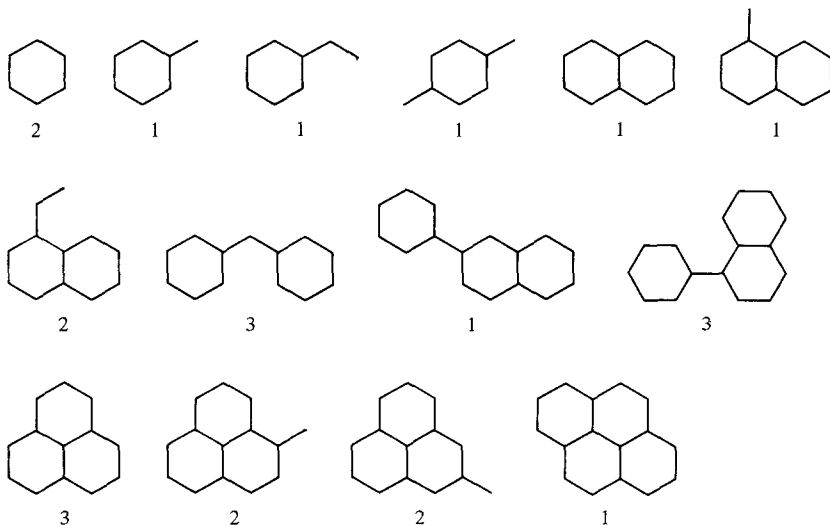


Fig. 13. Elementary graphs  $G'$  used for constructing subspectral benzenoid hydrocarbons by coalescence. Numbers below each graph show degeneracies of eigenvalues  $\pm 1$





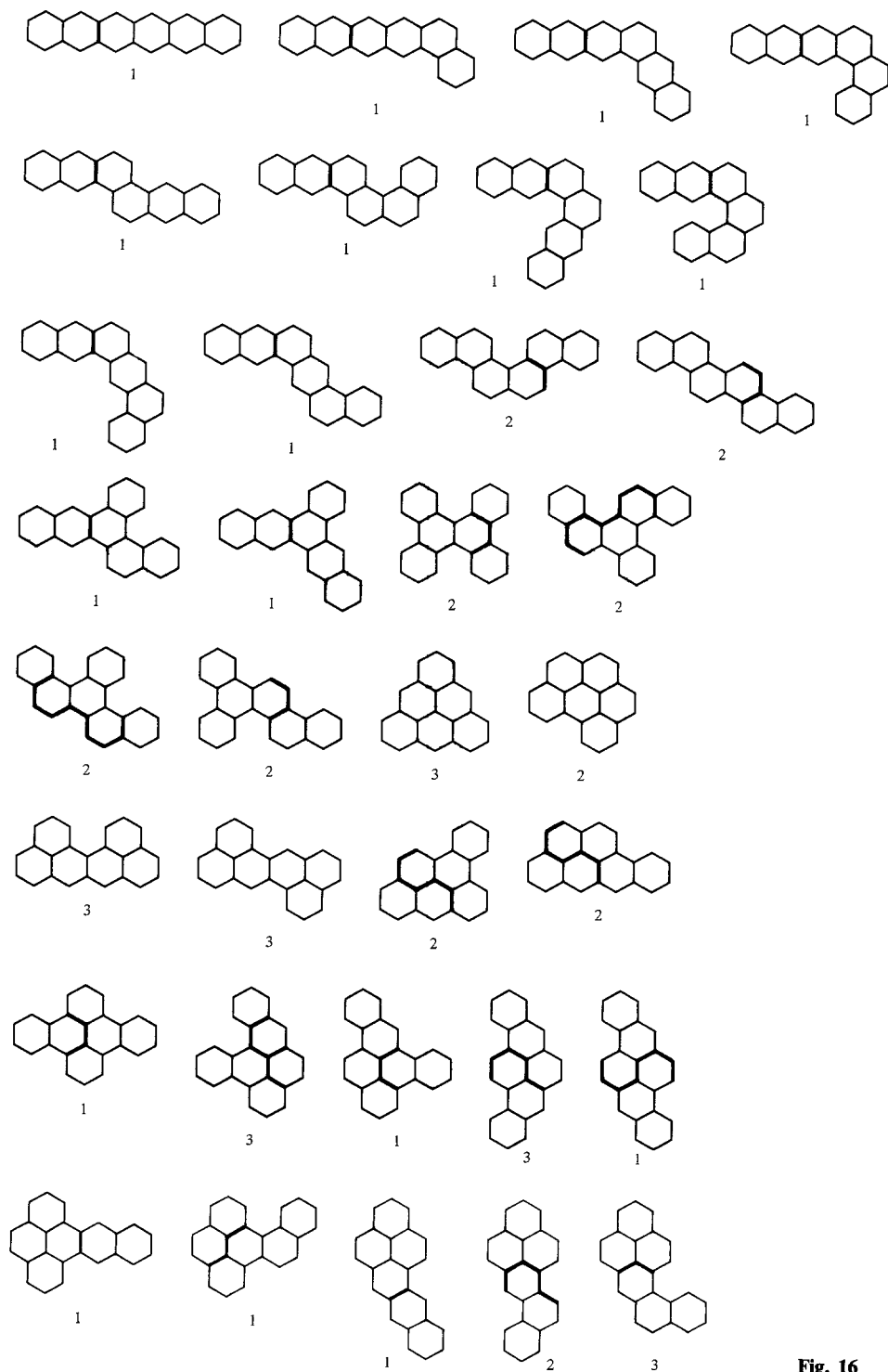
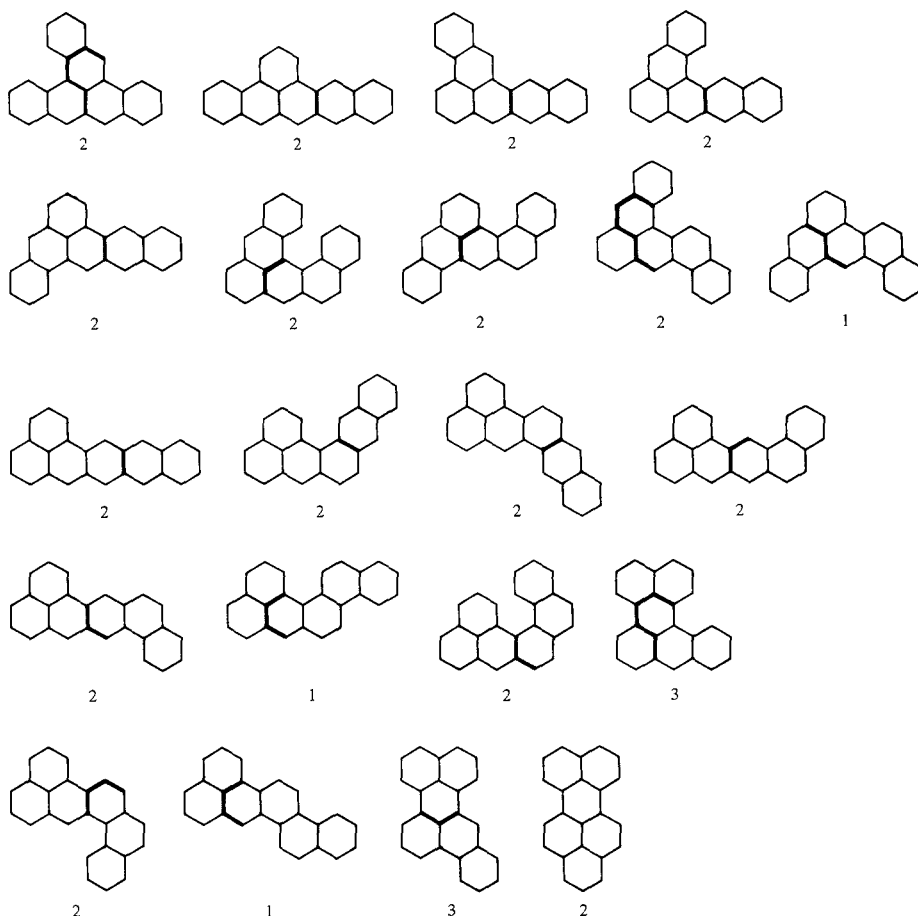


Fig. 16



**Fig. 16.** 6-Hexagonal benzenoid hydrocarbons sharing eigenvalues  $\pm 1$ ; numerals and heavy lines have the same meaning as in Fig. 15

## 5. Long chain polymers

For long chain benzenoid hydrocarbons, it is important to know the relationship between the degeneracy of the eigenvalue and chain length  $N$ , the number of repeated units. We have already given the results for two polymers (see Figs. 4, 12). Similarly, the investigation can readily be extended to many other polymers or homologous series, giving an insight into the density of states at  $x = \pm 1$  dependent on the topology and chain lengths. We present results rather than detailed calculations in accordance with Theorem 1 for simplicity; these polymeric series are displayed in Fig. 17, and the corresponding degeneracies listed in Table 2.

It is of interest to note that the number of states at  $x = \pm 1$  varies periodically in species I, VII, VIII and IX but increases in proportion to chain length  $N$

**Table 2.** Degeneracies at  $x = \pm 1$  varying with respect to chain length  $N$  for nine polymeric series. Roman numerals refer to the polymeric series depicted in Fig. 17

I		II					
$N$	$5n+1$	$5n+2$	$5n+3$				
$d$	2	1	0				
$N$	$5n+2$	$5n+3$	$5n+4$				
$d$	1	0	1				
$N$	$3n+1$	$3n+2$	$3n+3$				
$d$	3	2	1				
$N$	$3n+2$	$3n+3$	$3n+4$				
$d$	2	1	0				
III		IV		V			
$N$	$n$	$2n+1$	$2n$	$2n+1$	$2n+2$		
$d$	$n$	$2n$	$2n+1$	$2n+2$	$2n+1$		
VI		VII		VIII		IX	
$N$	$3n+1$	$3n+2$	$3n+3$	$7n+1$	$7n+2$	$7n+3$	$7n+4$
$d$	$3n+4$	$3n+3$	$3n+4$	1	1	2	2
$N$	$5n+1$	$5n+2$	$5n+3$	$5n+4$	$5n+5$	odd	even
$d$	1	1	0	2	0	2	0
$N$	$7n+1$	$7n+2$	$7n+3$	$7n+4$	$7n+5$	$7n+6$	$7n+7$
$d$	1	1	1	2	0	0	0

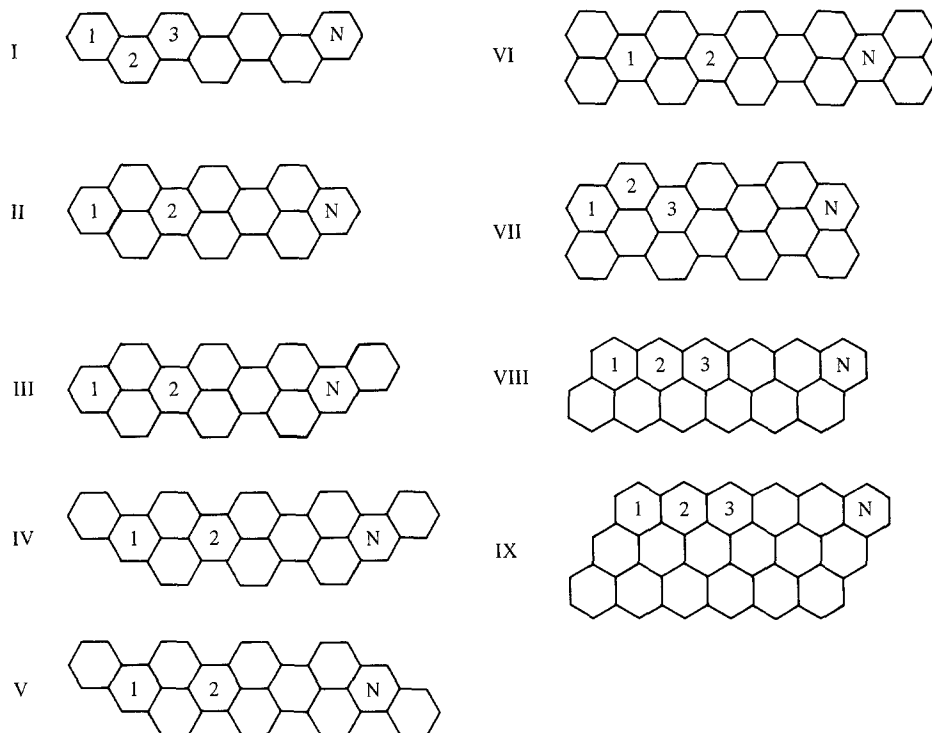


Fig. 17. Nine series of polymeric benzenoid hydrocarbons

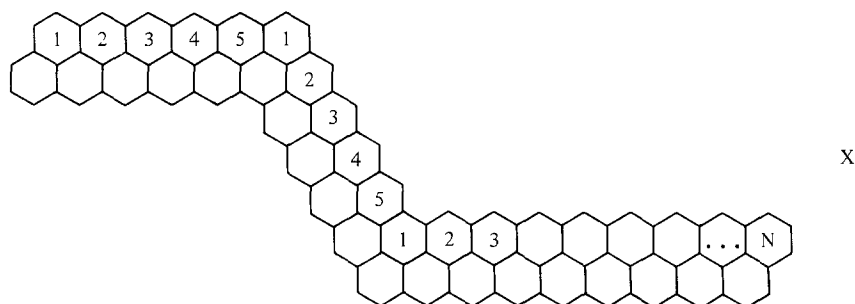


Fig. 18. Polymeric species having degeneracies of eigenvalues  $\pm 1$  similar to VIII

in other cases. The difference of terminal topology occurring among species II–VI influences the distribution of eigenvalues  $\pm 1$  significantly for finite  $N$  but negligibly for infinite  $N$ . The periodic appearance of eigenvalues  $\pm 1$  in a few polymers stimulates one to find additional subspectral series in which the periodicity of eigenvalues  $\pm 1$  still holds. For example, polymeric species X displayed in Fig. 18 have eigenvalues  $\pm 1$  with periodicity identical to VIII. On the other hand, the degeneracy at  $x = \pm 1$  increases in proportion to the chain

length  $N$  for species II, III, IV, V and VI, signifying the important role of the states around  $x = 1$  when a one-dimensional lattice is formed.

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