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REVIEW

FIBONACCI NUMBERS IN THE TOPOLOGICAL THEORY OF BENZENOID HYDROCARBONS AND RELATED GRAPHS

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Abstract

Fibonacci numbers are studied with respect to the topological theory of benzenoid hydrocarbons. These numbers are identified as the number of Kekulé structures of nonbranched all-benzenoid hydrocarbons, the number of matchings of paths, the number of independent sets of vertices of paths, the number of non-attacking rooks of certain rook boards, as well as the number of Clar structures of certain benzenoid hydrocarbons. Fibonacci numbers were also identified as the number of conjugated circuits of certain benzenoid hydrocarbons and thus they were also related to the structure-resonance model. Maximal independent sets of caterpillar trees are also shown to be Fibonacci numbers.

1. Introduction

The numbers 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, ... are known as the *Fibonacci numbers*. In his book *Liber Abaci* published in 1202, the Italian mathematician Leonard Fibonacci of Pisa posed the following problem [1]:

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> "Each month the female of a pair of rabbits gives birth to a pair of rabbits (of different sexes). Two months later the female of the new pair gives birth to a pair of rabbits. Find the number of rabbits in the beginning of the year."

The answer to this problem is 377 pairs of rabbits and every generation represents what is now called a Fibonacci number, as it is depicted below [2] in fig. 1. The name, Fibonacci numbers, was given by the nineteenth-century French mathematician Edouard Lucas [3].

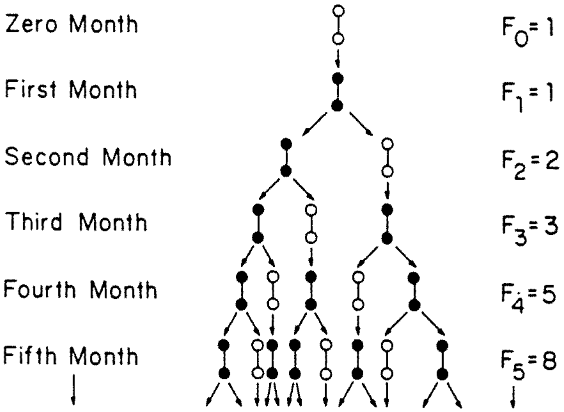


Fig. 1. Pictorial illustration of the "Rabbit Problem" that led to Fibonacci numbers. Bars with solid circles indicate a pair of rabbits ready for off-springs.

It is impossible to over-emphasize the importance and relevance of the Fibonacci numbers to the mathematical sciences and related areas. The interest in these numbers, which has grown rapidly during the present century, led the Soviet mathematician N. Vorobyov to publish his book [2] on Fibonacci numbers in 1961. In 1963, Hoggatt and his associates [3] founded *The Fibonacci Association* and began publishing *The Fibonacci Quarterly*.

In this review, we will emphasize the role of Fibonacci numbers in the topological theory of aromatic benzenoid hydrocarbons and their relation to the Clar sextet theory.

A rather popular result which connects Fibonacci numbers with benzenoid systems is the classical paper by Gordon and Davison [4], where it was demonstrated that the numbers of Kekulé structures (known in the mathematical literature as "linear factors" or "1-factors") of the zigzag polyacenes [4,5] are Fibonacci numbers. Although this review considers the role of Fibonacci numbers in polyhex and related graphs [6], we first very briefly mention other avatars of Fibonacci numbers. One quite early mention of these numbers was made by Cook in his book *The Curves of Life* [7], first published in 1914. He modeled the composition of the head of the giant sunflower by a series of spiral curves (on which the seeds are planned), forming a system of intersecting curves radiating from the center in such a manner that five such curves are turning in one direction and eight in the other, giving the results of intersection in a uniform sequence. Further, Cook suggested that "the only correct way of interpreting systems of intersecting curves is in terms of the number of curves radiating in each direction, and these numbers always occur in the Fibonacci series." The ratio of any successive pair of Fibonacci numbers is approximately constant, while as one goes up the series this ratio approaches a limit $= \frac{1}{2}(1 \pm \sqrt{5}) = \phi$. Cook observes that the inverse angle of ϕ of 360 degrees is $137^\circ\, 30'\, 27.95''$ and that if the leaves of a plant were set round a straight stem at a divergence angle of about $137^\circ\, 30'\, 28''$, no two leaves would ever be exactly superimposed on one another, which is the ideal situation for maximum light exposure. In fact, the angle $137^\circ\, 30'\, 27.95''$ is called "*Fibonacci* or *ideal angle*" in the sense of plant growth of spirally constructed flowers. Many other interesting facts might be inferred from the book by Cook [7], but here we will pursue the ratio ϕ in more detail: It is observed that the Fibonacci series might be viewed as a geometrical progression, the successive terms of which can be obtained by addition as well as by multiplication by the common ratio ϕ in the common way, i.e. $\phi^2 = \phi + 1$ or $\phi = \frac{1}{2}(1 \pm \sqrt{5}) \cong 1.618033988750$ or -0.618033988750. (In certain circumstances, the signs may be opposite and ϕ may have the four approximate values [7] $+1.618$, -1.618, $+0.618$ and -0.618, which remind us of the eigenspectrum of a path on four vertices [8].) The symbol ϕ was chosen partly because it is the first letter of Pheidias, in whose sculpture this proportion prevails when the distances between its salient points are measured. In fact, this ratio was originally called the "Ratio of Pheidias" [7], now known as the "Golden Mean" [9], and is defined to be the ratio of the length of the sides of a rectangle R which is similar to the rectangle R' remaining after cutting off a square section S of the parent R. Namely, let a and b, $a < b$, be the lengths of the sides of R and a' and b' be those of R', $a' < b'$. Naturally

$$\frac{b}{a} = \frac{b'}{a'} = \phi$$

and $a + a' = b$, while $b' = a$, so that

$$\phi^2 - \phi - 1 = 0,$$

which is essentially the auxiliary polynomial for the Fibonacci sequence (see eqs. 1–3 below). The golden mean ϕ is then $\frac{1}{2}(1 \pm \sqrt{5})$. An interesting point is that if one constructs a whole sequence of such rectangles R, R', R'',... they are evidently "self-similar", a feature in common with the quasicrystals [10,11] and their eigenvalue spectra. These quasicrystal models have a deterministic albeit not periodic structure. In the one-dimensional case, stage-n chains are obtained by joining stage-$(n-1)$ and stage-$(n-2)$ chains, and are sometimes called "*Fibonacci chains*". The two- and three-dimensional quasicrystal models are also often closely related, with dividing lines (in two-dimensional, or planes in three-dimensional) between cells spaced out in "accord" with the Fibonacci sequence. Burdett and Miller [12] model a quasi-periodic system of chains as being composed of two basic length scales L and S arranged in the sequence

$$SL\ SSL\ SL\ SSL\ SSL\ldots,$$

which has numerical similarities to the Penrose tiling [13]. In such a non-periodic pattern, one finds five interpenetrating sets of parallel lines passing through all vertices with spacings in the ratio $\phi:1 = 1.61803\ldots$: the golden mean.

A related concept known as *Fibonacci words* is discussed in *The Book of L* [14] and may be defined in the following way:

$$\begin{aligned} f_0 &= a \\ f_1 &= ab \\ f_2 &= aba \\ f_3 &= abaab \\ f_4 &= abaababa \\ &\vdots \\ f_{n+2} &= f_{n+1}\, f_n \qquad (n > 0). \end{aligned}$$

Zeckendorf's theorem [14] admits the representation of any integer n as a sum of Fibonacci numbers, viz. $n = F_{k_T} + F_{k_{T-1}} + \ldots + F_{k_1}$, where F_n is an nth Fibonacci number, taking $F_0 = F_1 = 1$, $F_2 = 2$, and $F_{n+2} = F_{n+1} + F_n$. Further, to any representation a word $a_{k_T} \ldots a_1 a_0$ is associated. For example, for $n = 128$ (in base 10) the words of the Fibonacci representations can be illustrated as follows:

F_{10}	F_9	F_8	F_7	F_6	F_5	F_4	F_3	F_2	F_1
1	0	1	0	0	0	1	0	0	0
1	0	1	0	0	0	0	1	1	0
1	0	0	1	1	0	1	0	0	0
1	0	0	1	1	0	0	1	1	0
1	0	0	1	0	1	1	1	1	0
	1	1	1	1	0	1	0	0	0
	1	1	1	1	0	0	1	1	0
	1	1	1	0	1	1	1	1	0

In the present review, we will not expose more details of such applications of Fibonacci numbers, but rather *restrict* our treatment to the role of these numbers in some of the combinatorial properties of polyhex and related graphs [6].

2. The Fibonacci recursive relation

An nth Fibonacci number is usually denoted by F_n:

$$F_n = F_{n-1} + F_{n-2} , \tag{1}$$

where $F_0 = F_1 = 1$. The recursion (1) defines the Fibonacci sequence $\{F_n\}$ shown in fig. 1 and truncated after the twelfth month. The Fibonacci numbers can be computed from their indices using the Binet formula (eq. (10)), which can be derived as follows: The general solution of eq. (1) is given by

$$F_n = \alpha\lambda_1^n + \beta\lambda_2^n , \tag{2}$$

where α and β are constants to be determined from initial conditions (i.e. F_0 and F_1) and the λ's are solutions of the auxiliary equation of (1), viz.,

$$\lambda^2 - \lambda - 1 = 0 . \tag{3}$$

Equation (3) has the following zeros:

$$\lambda_1 = (1 + \sqrt{5})/2; \quad \lambda_2 = (1 - \sqrt{5})/2 . \tag{4}$$

Therefore, eq. (2) can be rewritten as

$$F_n = \alpha \left(\frac{1 + \sqrt{5}}{2}\right)^n + \beta \left(\frac{1 - \sqrt{5}}{2}\right)^n . \tag{5}$$

The initial conditions require that

$$F_0 = \alpha + \beta = 1, \tag{6}$$

$$F_1 = 1 = \alpha \left(\frac{1 + \sqrt{5}}{2}\right) + \beta \left(\frac{1 - \sqrt{5}}{2}\right) . \tag{7}$$

Equations (6) and (7) can be solved for α and β to give

$$\alpha = \frac{1}{2}\left(\frac{\sqrt{5}-1}{\sqrt{5}}\right) \tag{8}$$

$$\beta = \frac{1}{2}\left(\frac{1+\sqrt{5}}{\sqrt{5}}\right). \tag{9}$$

When eqs. (8) and (9) are used in eq. (5), one obtains the Binet formula, viz.,

$$F_n = \frac{1}{\sqrt{5}}\left[\left(\frac{1+\sqrt{5}}{2}\right)^{n+1} - \left(\frac{1-\sqrt{5}}{2}\right)^{n+1}\right]. \tag{10}$$

3. Generation of Fibonacci numbers in chemistry

3.1. KEKULÉ STRUCTURES OF THE "FIBONACCENES"

One of the earliest counts in chemistry which lead to Fibonacci numbers is the number of Kekulé structures of the zigzag polyacenes, i.e. phenanthrene, chrysene, picene, fulminene, etc., whose numbers of Kekulé structures are, respectively, 5, 8, 13, 21 representing F_4, F_5, F_6, F_7, respectively (fig. 2).

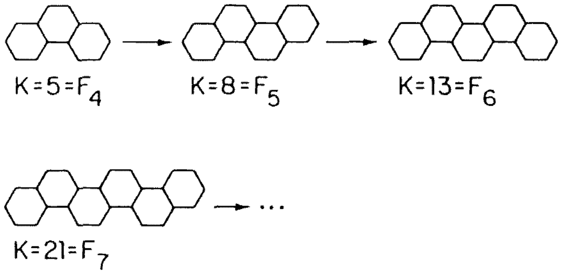


Fig. 2. The first few members of the fibonaccenes (i.e. non-branched all-benzenoid hydrocarbons). K's are numbers of their Kekulé structure which are Fibonacci numbers.

In fact, these hydrocarbons have recently been called "fibonaccenes" [15]. Thus, if we let $K(A_j)$ be the number of Kekulé structures of a member of the fibonaccenes containing j rings [16], one can write

$$K(A_{j+2}) = K(A_{j+1}) + K(A_j), \quad j \geqslant 1 \tag{11}$$

$$K(A_j) = F_{j+1}$$

(of course, $j = 1$ represents benzene, $j = 2$ naphthalene, $j = 3$ phenanthrene and so on). Equations (1) and (11) are isomorphic.

The sextet polynomial

In 1975, Hosoya and Yamaguchi [17] published an elegant combinatorial description of the resonance relations among the individual hexagons of benzenoid hydrocarbons. Thus they defined for the first time their Sextet Polynomial $B_G(x)$ for a benzenoid hydrocarbon as:

$$B_G(x) = \sum_{k=0}^{m} r(G,k)\,x^k , \tag{12}$$

where $r(G,k)$ is called the kth resonant number: it enumerates the number of selections of k mutually resonant [18] but disjoint rings in the benzenoid system B; $r(G,0)$ is defined to be unity and m is the maximal value of k. The sextet polynomials of the fibonaccenes are particularly interesting. We list such polynomials for the first few members (R = number of rings) in table 1. Several interesting properties

Table 1

Sextet polynomials of the first few members of the fibonaccenes

R	$B_G(x)$	$B_G(1)$
1	$\binom{2}{0} + \binom{1}{1}x$	$2 = F_2$
2	$\binom{3}{0} + \binom{2}{1}x$	$3 = F_3$
3	$\binom{4}{0} + \binom{3}{1}x + \binom{2}{2}x^2$	$5 = F_4$
4	$\binom{5}{0} + \binom{4}{1}x + \binom{3}{2}x^2$	$8 = F_5$
5	$\binom{6}{0} + \binom{5}{1}x + \binom{4}{2}x^2 + \binom{3}{3}x^3$	$13 = F_6$
6	$\binom{7}{0} + \binom{6}{1}x + \binom{5}{2}x^2 + \binom{4}{3}x^3$	$21 = F_7$
7	$\binom{8}{0} + \binom{7}{1}x + \binom{6}{2}x^2 + \binom{5}{3}x^3 + \binom{4}{4}x^4$	$34 = F_8$

are evident. First, the individual terms, i.e. $r(G, j)$'s, are binomial coefficients which generate the Pascal triangle [19]. Second, the resonant numbers recur in the following manner:

$$r(G_n, j) + r(G_{n+1}, j+1) = r(G_{n+2}, j+1), \tag{13}$$

which is isomorphic to eq. (11). Third, the sextet polynomials of this particular class generate Fibonacci numbers when $x = 1$. Naturally, for a given fibonaccene containing R rings one can write [20]:

$$r(G; j) = \binom{R+1-j}{j}. \tag{14}$$

The transfer matrix [21,22]

Fibonacci numbers might also be generated using various powers of the transfer matrices [21,22] describing double bond positions in fibonaccenes. This is shown in fig. 3 for naphthalene, phenanthrene and a regular network. Each of the Kekulé valence bond structures labelled by a sequence of local states specified at the dotted-line positions. The letters S and D stand for single and double bonds, respectively. Thus, SS means that the local state is defined by single bonds where the dotted line crosses the edges of a hexagon and so on. From fig. 3, it is clear that for naphthalene the SS state leads to either a DD or an SS state, while a DD initial state can generate only another DD state. Thus, one may write a transfer matrix T_2 for naphthalene:

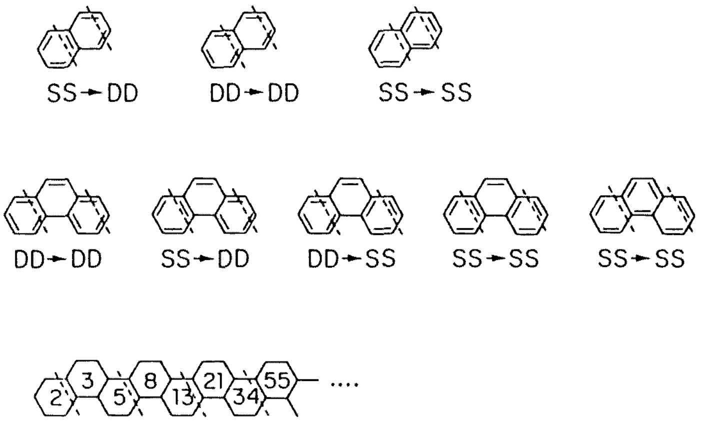


Fig. 3. Local states of transfer matrices leading to Fibonacci numbers

$$T_2 = \begin{array}{c|cc} & SS & DD \\ SS & 1 & 1 \\ DD & 0 & 1 \end{array} . \tag{15}$$

Similarly, for phenanthrene one has:

$$T_3 = \begin{array}{c|cc} & SS & DD \\ SS & 2 & 1 \\ DD & 1 & 1 \end{array} . \tag{16}$$

Various powers of T_3 generate 5, 13, 34,... (the numbers are the sums of the matrix elements which are F_5, F_7, F_9,...), while combinations of T_2 and T_3 generate other Fibonacci numbers. For example:

$$T_2\, T_3 = \begin{pmatrix} 2 & 3 \\ 1 & 2 \end{pmatrix} \rightarrow 8 = F_5 \tag{17}$$

$$T_3\, T_3\, T_2 = \begin{pmatrix} 5 & 8 \\ 3 & 5 \end{pmatrix} \rightarrow 21 = F_7, \tag{18}$$

and so on.

A special family of branched benzenoid hydrocarbons

In fig. 4, we show two families of branched all-benzenoid systems. The Kekulé counts of such families can be expressed as simple functions of Fibonacci numbers. Thus, one can easily write the following identities [11] (some illustrations are shown in fig. 4):

$$K(A_{11}) = F_4 + F_2\, F_3 \tag{19}$$

$$K(A_{12}) = F_5 + F_2\, F_3 \tag{20}$$

$$K(A_{13}) = F_6 + F_2\, F_3 \tag{21}$$

$$K(A_{14}) = F_7 + F_2\, F_5\ , \tag{22}$$

and so on. Similarly, for the second family (with two branched centers) we can write:

$$K(A_1\, A_1) = F_5 + F_2\, (F_3 + F_4) \tag{23}$$

$$K(A_1\, A_{12}) = F_6 + F_2\, (2F_4 + F_2 \cdot F_2) \tag{24}$$

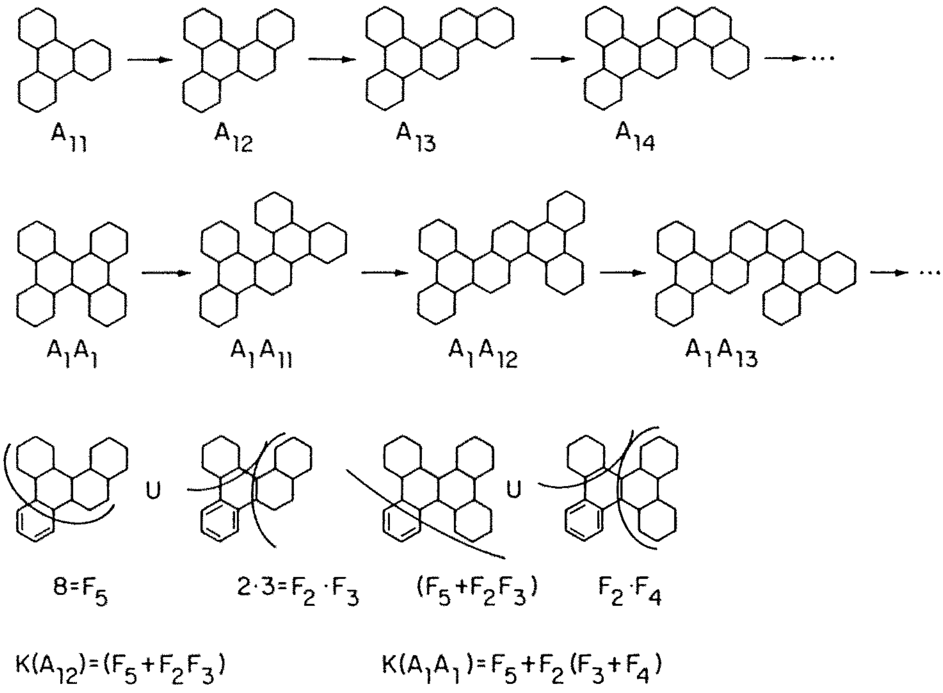


Fig. 4. Two families of branched all-benzenoid hydrocarbons. The last line illustrates recursive generation of the number of their Kekulé structures expressed as sums of Fibonacci numbers.

$$K(A_1 A_{13}) = F_7 + F_2 \, (2F_5 + F_2 \cdot F_3) \tag{25}$$

$$K(A_1 A_{14}) = F_8 + F_2 \, (2F_6 + F_2 \, F_4) \tag{26}$$

and similarly for higher members.

3.2. THE COUNTING POLYNOMIAL OF HOSOYA [23]

During his study of the topological nature of structural isomers of saturated hydrocarbons, Hosoya [23] defined a counting polynomial $H(G;x)$ of a molecular graph G by an equation isomorphic to eq. (12), namely:

$$H(G:x) = \sum_{k=0}^{m} p(G,k)x^k. \tag{27}$$

The numbers $p(G,k)$'s are known as the number of k-matchings of G and their sequence is called the sequence of "nonadjacent numbers" of G. In general, a number

Table 2

Counting polynomials $H(G;\, x)$'s and topological indices of the paths (L_n = path on n vertices)

n	$H(G = L_n; x)$	$Z_{G=L_n}$
2	$1 + x$	$2 = F_2$
3	$1 + 2x$	$3 = F_3$
4	$1 + 3x + x^2$	$5 = F_4$
5	$1 + 4x + 3x^2$	$8 = F_5$
6	$1 + 5x + 6x^2 + x^3$	$13 = F_6$
7	$1 + 6x + 10x^2 + 4x^3$	$21 = F_7$
8	$1 + 7x + 15x^2 + 10x^3 + x^4$	$34 = F_8$

Table 3

Independence polynomials $W(L;\, x)$'s of the first few paths (L_n is a path on n vertices)

n	$W(L_n; x)$	$W(L_n; 1)$
1	$1 + x$	2
2	$1 + 2x$	3
3	$1 + 3x + x^2$	5
4	$1 + 4x + 3x^2$	8
5	$1 + 5x + 6x^2 + x^3$	13
↓		↓

$p(G, j)$ is the number of selections of j disconnected edges in G, where by definition $p(G, 1) = 0$. A toplogical index Z_G is defined [12] to be:

$$Z_G = H(G; 1) = \sum_{k=0}^{m} p(G, k). \tag{28}$$

The counting polynomials of the first few members of the normal alkanes for which their molecular graphs are paths are given in table 2. We observe that the polynomials of tables 2 and 3 are identical. Furthermore, the topological indices of the paths generate the Fibonacci sequence [24].

3.3. THE INDEPENDENCE POLYNOMIAL [25]

In his study of the topological properties of benzenoid systems, Gutman [25] defined the independence polynomial of G, $W(G;x)$ as:

$$W(G;x) = \sum_{k=0}^{m} \mathrm{O}(G,k)x^k . \tag{29}$$

The coefficients $\mathrm{O}(G,k)$'s count the number of choices of k nonadjacent vertices in G, again defining $\mathrm{O}(G,0) = 1$. Table 2 lists such polynomials for the first few paths. In a recent paper, Balasubramanian and Ramaraj [26] considered the independence polynomial under the name color polynomial.

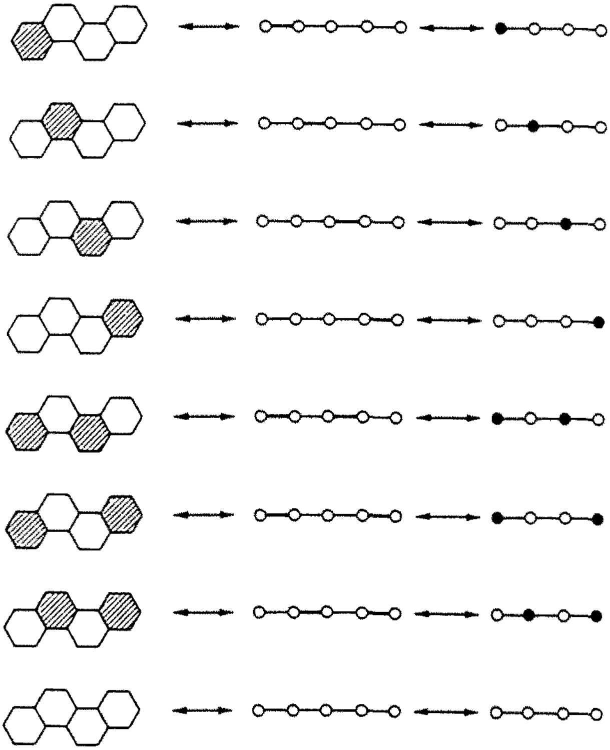


Fig. 5. Graphical generation of F_5. One-to-one mapping between $r(G,k)$, $p(G,k)$, and $\mathrm{O}(G,k)$. Cf. eqs. (12), (27) and (29), respectively.

Figure 5 illustrates a one-to-one correspondence between nonadjacent *hexagons* (resonance relations [23]), nonadjacent *edges* and nonadjacent *vertices*.

3.4. ROOK POLYNOMIALS [27,28]

A rook polynomial is a combinatorial descriptor of the adjacency relations of the cells in a rook board [27]. The latter is a subset of a $j \times j$ chessboard. A "chemical version" of these objects can be found in the work of Godsil and Gutman [28]. A rook polynomial $R(G, x)$ can be defined analogously with sextet, counting and color (independence) polynomials (eqs. (12), (27) and (29), respectively). Thus:

$$R(G, x) = \sum_{k=0}^{m} \varphi(G, k) x^k \, . \tag{30}$$

Again, $\varphi(G, k)$ enumerates the number of selections of k nonadjacent *cells* in the rook board, where $\varphi(G, 0) = 1$. Here, two cells are defined to be adjacent if they share a common row or column in the board and nonadjacent otherwise. Based on this definition, one can construct rook boards which generate Fibonacci numbers (i.e. whose $R(G, 1)$'s are Fibonacci numbers). Figure 6 shows a few such boards.

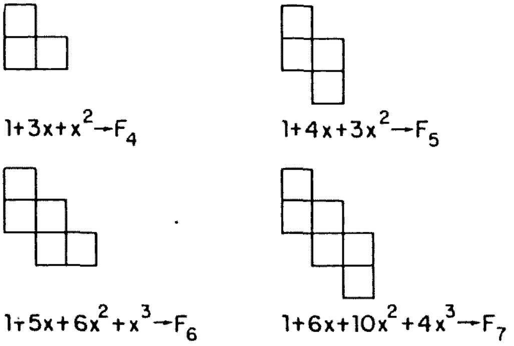
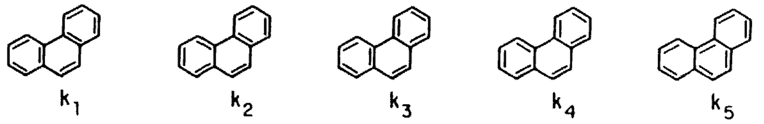


Fig. 6. Rook polynomials generating Fibonacci numbers.

3.5. THE PERMUTATION INTEGRALS (OF HERNDON [29]) AND THE CONJUGATED CIRCUITS (OF RANDIĆ [30])

In his structure-resonance theory, Herndon [29] defined a permutation integral to indicate the permutation of $(4i + 2)$ pi-electrons between two Kekulé valence structures belonging to a given benzenoid system. A count γ_i of these integrals for a given hydrocarbon predicts its stability. Furthermore, twice these integral counts gives counts of conjugated circuits (of Randić [30]), i.e. $2\gamma_i = R_i$, where R_i counts conjugated circuits involving $(4i + 2)$ pi-electrons. Figure 7 shows the five Kekulé structures of phenanthrene and superpositions for the associated permutation integrals. There one finds $\gamma_1 = 5$, $\gamma_2 = 2$, and $\gamma_3 = 1$ (and thus, $R_1 = 10$, $R_2 = 4$, and $R_3 = 2$) for



$$\begin{array}{c|ccccc} & k_1 & k_2 & k_3 & k_4 & k_5 \\ \hline k_1 & 0 & \gamma_1 & \gamma_1 & 0 & \gamma_1 \\ k_2 & & 0 & 0 & \gamma_1 & \gamma_2 \\ k_3 & & & 0 & \gamma_1 & \gamma_2 \\ k_4 & & & & 0 & \gamma_3 \\ k_5 & & & & & 0 \end{array}$$

Fig. 7. Permutation pi-electrons of phenanthrene.

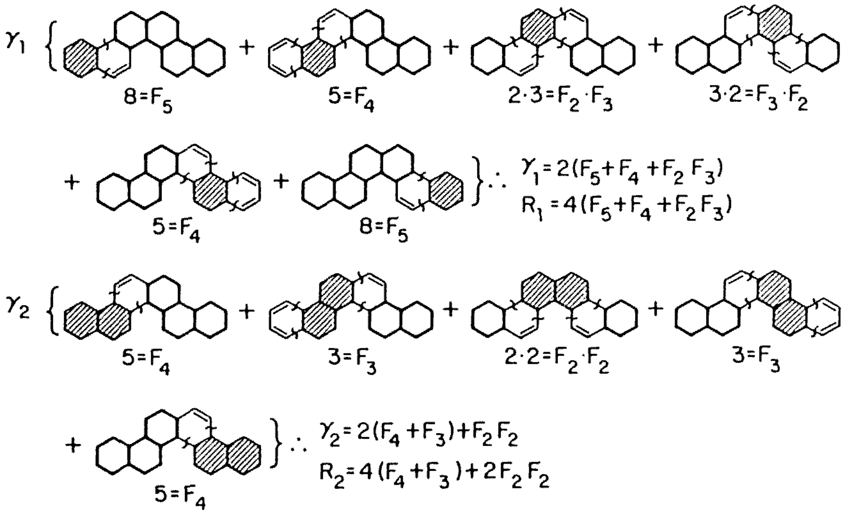


Fig. 8. Graphical computation of R_2 and γ_2 of fulminene in units of Fibonacci numbers.

phenanthrene. There is a graphic way of enumerating these parameters [31,29]. For example, to calculate γ_1 choose any hexagon in the system, delete this hexagon together with all edges incident with it, and calculate K for the remaining fragment. The process is repeated over all hexagons. Then γ_1 is the sum of all K's. For γ_2, two adjacent hexagons are removed at a time, and so on. The process is illustrated in fig. 8 for the "sixth member" of the fibonaccenes (fulminene). In fig. 9, we illustrate

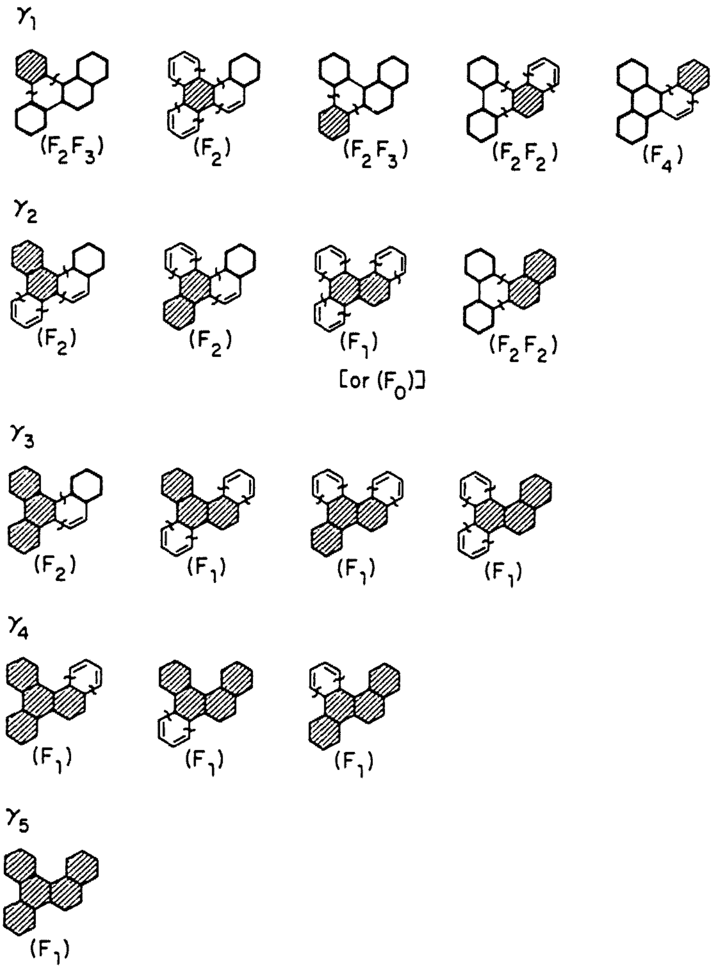


Fig. 9. Graphical enumeration of all γ's for a branched all-benzenoid. Counts are given in terms of Fibonacci numbers.

how to obtain permutation integrals γ's for a branched system in the units of Fibonacci numbers.

Table 4 shows all permutation integrals (and hence, also conjugated circuits) for several fibonaccenes. It is interesting to observe diagonal indentities [32] such as:

$$\gamma_1(3) = \gamma_2(4) = \gamma_3(5) = \ldots$$

$$\gamma_2(3) = \gamma_3(4) = \gamma_4(5) = \ldots ,$$

or in general

Table 4

Permutation integrals (γ's) and conjugated circuits (R's) of the non-branched zigzag fibonaccenes in units of Fibonacci numbers. Observe diagonal identity

Number of rings	$\gamma_1 = \frac{1}{2} R_1$	$\gamma_2 = \frac{1}{2} R_2$	$\gamma_3 = \frac{1}{2} R_3$	$\gamma_4 = \frac{1}{2} R_4$	$\gamma_5 = \frac{1}{2} R_5$	$\gamma_6 = \frac{1}{2} R_6$	$\gamma_7 = \frac{1}{2} R_7$
3	$(F_1 + 2F_2)$	$2F_1$	F_1				
4	$2(F_2 + F_3)$	$(F_1 + 2F_2)$	$2F_1$	F_1			
5	$2(F_3 + F_4) + F_2^2$	$2(F_2 + F_3)$	$(F_1 + 2F_2)$	$2F_1$	F_1		
6	$2(F_2 F_3 + F_4 + F_5)$	$2(F_3 + F_4) + F_2^2$	$2(F_2 + F_3)$	$(F_1 + 2F_2)$	$2F_1$	F_1	
7	$2(F_2 F_4 + F_5 + F_6) + F_3^2$	$2(F_2 F_3 + F_4 + F_5)$	$2(F_3 + F_4) + F_2^2$	$2(F_2 + F_3)$	$(F_1 + 2F_2)$	$2F_1$	F_1

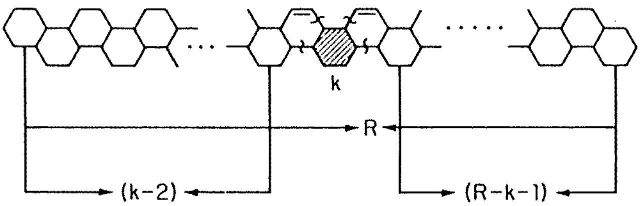
$$\gamma_i(R) = \gamma_{i+1}(R+1), \tag{31}$$

where $\gamma_i(R)$ counts ith permutation integrals of a fibonaccene containing R rings. Equation (31) is discussed in ref. [32].

A closed form for obtaining $\gamma_i(R)$ in terms of Fibonacci numbers is given by [32]

$$\gamma_i(R) = \sum_{k-1}^{n+1-i} F_{n+1-i-k} F_{k-1} \, . \tag{32}$$

To understand eq. (32), let us first calculate $\gamma_1(R)$ for a general fibonaccene as shown below:



The length of the fibonaccene is R and we choose any arbitrary hexagon k, remove this hexagon and all edges incident to it and then the number of Kekulé structures of the remaining (disconnected) fibonaccene will be $K(A_{k-2}) \cdot K(A_{R-k-1})$ or, applying eq. (11), $(F_{k-1} \cdot F_{R-k})$. Now to obtain γ_1 one must repeat the above operation over all hexagons in the fibonaccene. Then we can write:

$$\gamma_1(R) = \sum_{k=1}^{R} F_{k-1} F_{R-k} \, . \tag{33}$$

Next, we calculate $\gamma_i(R)$ in terms of $\gamma_1(R)$. To do this, we apply the diagonal identity, eq. (31), to give:

$$\gamma_i(R) = \gamma_1(R+1-i) \, . \tag{34}$$

Applying (34) and (33), we obtain the desired expression, eq. (32). A more formal elaboration of this subject is found in ref. [32]. Table 5 lists some γ values for some branched all-benzenoid systems in units of Fibonacci numbers.

Table 5

Branched all-benzenoid hydrocarbons with one branched center (fig. 4). Numbers in parentheses (from left to right) indicate $\gamma_1, \gamma_2, \ldots$, i.e. number of permutation integrals involving $6, 10, \ldots$, pi-electrons, respectively, in units of Fibonacci numbers

A11

$(F_1 + 3F_2^2)$, $(3F_1)$, $(2F_1)$, (F_1)

A12

$(F_2 + F_2^2 + 2F_2F_3 + F_4)$, $(F_1 + 2F_2 + F_2^2)$, $(3F_1 + F_2)$, $(3F_1)$, (F_1)

A13

$(2F_2^2 + 2F_2F_4 + F_3 + 2F_4)$, $(F_2 + F_2 + F_3 + F_4)$, $(F_1 + 2F_2 + F_2^2 + F_3)$,
$(3F_1 + F_2)$, $(3F_1)$, (F_1)

A14

$(F_2F_3 + F_2F_4 + 2F_2F_5 + F_2^2F_3 + F_2^2F_4 + F_4 + F_5)$, $(2F_2^2 + F_3 + 4F_4)$,
$(F_2 + F_2^2 + 2(F_3 + F_4))$, $(F_1 + 2F_2 + F_2^2 + F_3)$, $(3F_1 + F_2)$, $(3F_1)$, (F_1)

3.6. MAXIMAL INDEPENDENT SETS OF THE VERTICES OF A CATERPILLAR TREE AND KING POLYNOMINO GRAPHS

The vertices of a graph can, in general, be partitioned into a finite number of sets. A set of vertices in which no two vertices are adjacent is called an *independent* set of vertices. An independent set of vertices $\{V(r)\}$ in G is said to be *maximal* [33] if every vertex of $G \notin \{V(r)\}$ is adjacent to at least one of the r verties of $\{V(r)\}$. One of the authors of ref. [34] has recently demonstrated that the maximal independent sets of the vertices of a caterpillar tree [35–39] $T_l(i, j, k, \ldots, m)$, where $l, i, j, k, \ldots, m$ are all >0, generate Fibonacci numbers. First we define $T_l(i, j, k, \ldots, m)$: it is a tree formed from a path on l vertices by the addition of $i, j, k, \ldots, m$ monovalent vertices to its first, second, ..., lth vertex. For example, the tree shown in fig. 10 is $T_4(3, 1, 1, 2)$. Let the number of maximal independent sets of $T_l(i, j, k, \ldots, m)$ be ζ_l; then the following result was proved [34]:

$$\zeta_l = F_{l+1} \tag{35}$$

and thus

$$\zeta_{l+2} = \zeta_{l+1} + \zeta_l \,. \tag{36}$$

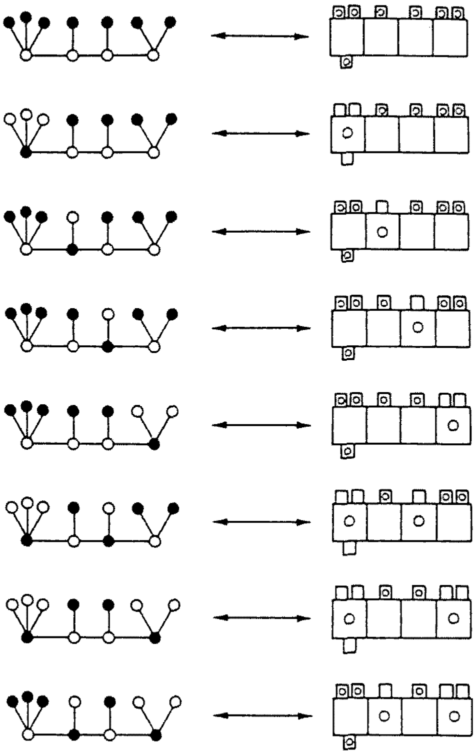


Fig. 10. All maximal independent sets of vertices of T_4 (3, 1, 1, 2) and the corresponding king polyominos. The set generates $F_5 = 8$.

In fig. 10, the eight maximal independent sets of the vertices of T_4 (3, 1, 1, 2) are shown on the left. These sets can be obtained by coloring the vertices in black and white (or any two different colors) such that:

(a) no two black vertices are adjacent, and

(b) every white vertex is adjacent to at least one black vertex.

The number 8 is equal to F_5, which is in agreement with eq. (35). The latter equality is proved in ref. [34]. The proof might be approached in many ways, the easiest of which involves distinguishing the root vertices (i.e. those making the backbone of the caterpillar) from the monovalent vertices (which make its "feet"). It is clear from rules (a) and (b) that the "feet" attached to any white root vertex must be black and the "feet" attached to any black vertex must be white. Thus, the problem reduces to finding the number of selections of k independent vertices of the backbone for $0 \leqslant k \leqslant l$, l being the number of root vertices. Such counts are given [25] the symbol $O(G, k)$, cf. eq. (29), and they constitute the terms of the independence polynomial [25] (which is also called the coloring polynomial [26]).

These trees are the dualist graphs [40] of certain polyominos [41]. For the particular caterpillar T_4 (3, 1, 1, 2), the polyomino graphs shown on the right-hand side of fig. 10 correspond to individual maximal independent sets. The set of polyominos shown in fig. 10 represent the so-called king pattern [41], i.e. the number of ways of placing k non-attacking kings (i.e. no two kings in two adjacent cells) on the polyomino board. From fig. 10, it can be concluded that there are three ways of placing seven non-attacking kings, two ways of placing six or five non-attacking kings, but only one way in which one can distribute four non-attacking kings on this particular polyomino graph. Again, the total number of ways is eight, which is F_5.

3.7. CLAR STRUCTURE COUNT OF CERTAIN BENZENOID HYDROCARBONS

Figure 11 shows a homologous series of benzenoid hydrocarbons denoted as $B(T_{n,1})$'s. We observe that the dualist of $B(T_{n,1})$ is simply the caterpillar tree $T_{n,1}$. Since maximal independent sets of vertices of such trees generate Fibonacci numbers (cf. section 3.6), one expects that the number of Clar structures in which maximum numbers of hexagons are assigned to have resonant sextets conforms to eqs. (35) and (36), i.e.

$$\zeta(B(T_{n,1})) = F_{n+1}; \tag{35}$$

$$\zeta(B(T_{n+2,1})) = \zeta(B(T_{n+1,1})) + \zeta(B(T_{n,1})), \tag{36}$$

where $\zeta(B(T_{n,1}))$ is the number of Clar structures of $B(T_{n,1})$. This result may be understood by mapping the vertices of $T_{n,1}$ onto the hexagons of $B(T_{n,1})$ where, say, black vertices correspond to hexagons with Clar circles and white vertices to hexagons without circles. Figure 12 shows all five (= F_4) Clar structures of $B(T_{3,1})$.

4. Summary and conclusions

Fibonacci numbers define counts of several combinatorial objects related to the topological theory of benzenoid hydrocarbons as well as the Clar sextet theory. In particular, enumeration of the following leads to Fibonacci numbers:

(1) The number of Kekulé structures of nonbranched all-benzenoid hydrocarbons.

(2) The total number of matchings of the edges of a path tree.

(3) The total number of independent sets of vertices of paths.

(4) The number of non-attacking rooks of certain rook boards.

(5) The number of Clar structures of certain benzenoid hydrocarbons.

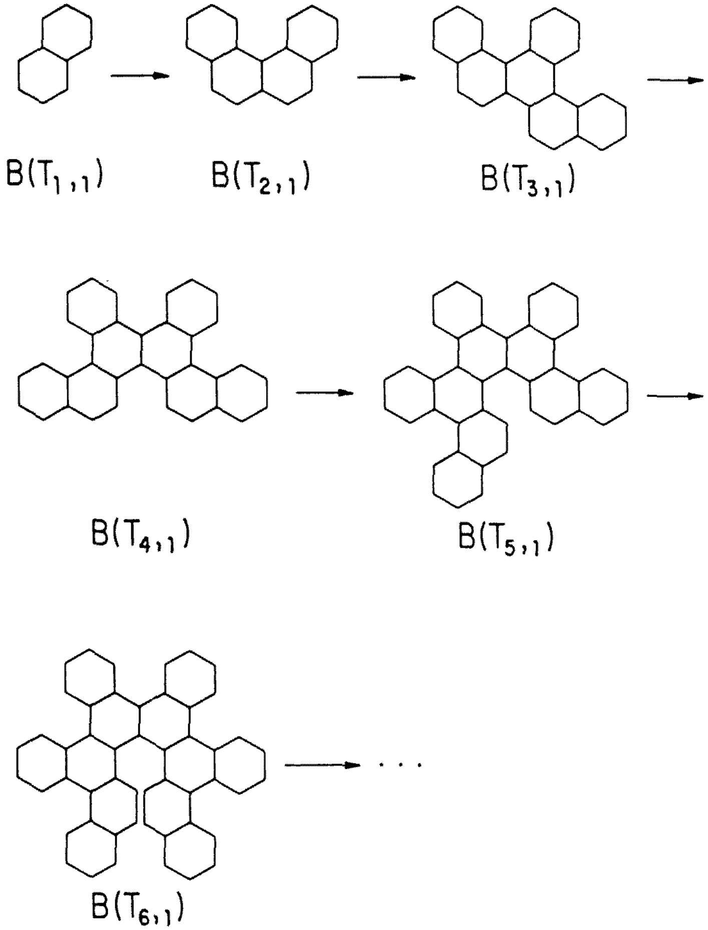


Fig. 11. A family of benzenoid hydrocarbons whose Clar counts are Fibonacci numbers (see fig. 12).

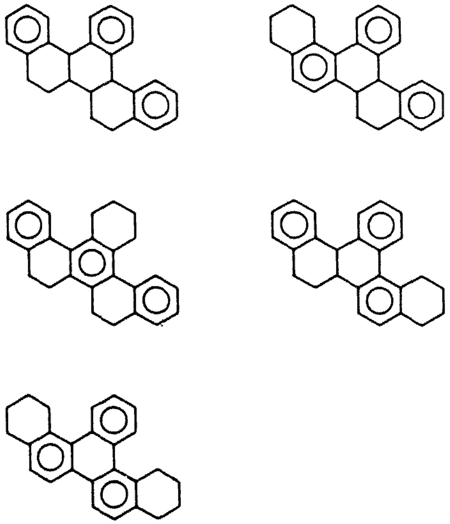


Fig. 12. All five ($=F_4$) Clar structures of $B(T_{3,1})$.

(6) The number of maximal independent sets of any caterpillar tree of the form $T_l(m_1, m_2, \ldots, m_l)$, where all m's $\geqslant 1$.

In addition, the number of conjugated circuits (and thus permutation pi-electron integrals) of all-benzenoid hydrocarbons can be expressed as simple functions of Fibonacci numbers.

It is worth noting that Fibonacci numbers were also obtained as the number of dimer coverings (i.e. Kekulé structures) on ladder graphs. Here, the latter graphs are equivalent to the fibonaccenes. Further, the Fibonacci recurrence such as eq. (11) is independent of the ends appended to the fibonaccene chain (as long as the ends involve appending an *even* number of sites to the ends), an observation which seems to have been first reported by Cyvin and Gutman [42], who also note that another form of eq. (11) viz.,

$$K(A_{j+2}) = K(A_1)F_{j+1} + K(A_0)F_j \,. \tag{37}$$

(where $K(A_0) = 1$). Equation (37) represents what is called a "double Fibonacci sequence" [7].

Recently, Klein and Seitz [43] have shown that "*similar*" forms of eqs. (19)–(26) actually apply to *any* catacondensed benzenoid hydrocarbon.

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