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ON POLYMETHINE GRAPHS

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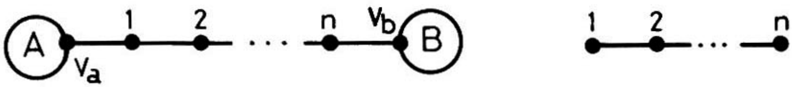
Abstract

The molecular graphs of general α,ω-disubstituted polymethines are examined and a number of their mathematical properties are indicated. Some interesting topological characteristics of this class of conjugated pi-electron systems are presented.

Introduction

In this paper we shall consider α,ω-disubstituted polymethines, whose general formula is $A-(CH)_n-B$, while A and B denote arbitrary conjugated fragments. Such pi--electron systems are represented by molecular graphs G_n of the following structure.

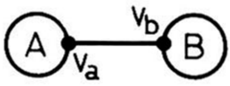


G_n P_n

Hence, a polymethine graph G_n is constructed by attaching two arbitrary molecular graphs A and B to the terminal vertices of the path P_n with n vertices. Let the path P_n be joined to the vertex v_a of A and to the vertex v_b of B.

Our discussion will also include the case when the graphs A and/or B coincide with the empty graph $\emptyset$. If both $A = \emptyset$ and $B = \emptyset$, then $G_n = P_n$.

If not stated otherwise, our results and equations hold for all $n = 0,1,2,...$ Of course, $P_0 = \emptyset$ and G_0 is a graph obtained by joining the vertex v_a of A to the vertex v_b of B.



G_o

Throughout the present work we will be mainly interested in the characteristic polynomials of the pertinent graphs. For reasons of simplicity the characteristic polynomial of a graph G will be denoted also by G or G(x). In addition, it is both consistent and convenient to assert that the characteristic polynomial of the empty graph Ø is equal to unity, while the characteristic polynomial of $A-v_a$ is equal to zero if $A = \emptyset$.

Although in the past the polymethines were subject to a variety of theoretical and quantum chemical examinations, the real impetus for the investigation of the topological properties of this class of conjugated compounds came from the work of Fabian and Hartmann.[1,2] Namely, they made the remarkable discovery that in certain polymethines all bond orders (between adjacent atoms) are mutually equal. Polymethine graphs representing such molecules are P_n^{++} and P_n^{--}, i.e. the subgraphs A and B in P_n^{++} (resp. P_n^{--}) consist of a single vertex with a self-loop of the weight +1 (resp. -1).

P_n^{++} P_n^{--}

One should realize that there are no symmetry reasons for the equality of the bond orders in P_n^{++} and P_n^{--}, hence this is a purely topological phenomenon.*

<u>The recurrence relation for the characteristic polynomial of polymethine graphs</u>

It is well known[3] that the characteristic polynomial of the path P_n conforms to the following recurrence relation.

$$P_n = x\ P_{n-1} - P_{n-2}$$

It was, however, long time overlooked that an equivalent

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* One should compare the finding of Fabian and Hartmann with Coulson - Rushbrooke's pairing theorem, which has the consequence that all pi-electron charge densities in alternant hydrocarbons are mutually equal.

relation is valid for all polymethine graphs, namely

$$G_n = x\, G_{n-1} - G_{n-2} \tag{1}$$

irrespective of the nature of the terminal groups A and B. This result seems to be first published in 1976.[4]

Eq. (1) is important for several reasons. First, since it holds for all polymethine graphs, it represents just an algebraic consequence of the fact that the path P_n is contained in G_n as a fragment. Furthermore, if G_n symbolizes a graph with N+n vertices for $n = 0,1,2,\ldots,$ then G_n is a polymethine graph if and only if eq. (1) is fulfilled for $n = 2,3,\ldots$.

Second, from (1) the explicite form of $G_n(x)$ can be determined[4], viz.,

$$G_n = G_1\, P_{n-1} - G_0\, P_{n-2}$$

Third, simple general analytic expressions for the characteristic polynomials of certain polymethine graphs have been deduced from eq. (1), namely

$$P_n = \sin(n+1)t \, / \, \sin t \tag{2 a}$$

$$P_n^+ = \cos \frac{(2n+3)t}{2} \, / \, \cos(t/2) \tag{2 b}$$

$$P_n^- = \sin \frac{(2n+3)t}{2} \, / \, \sin(t/2) \tag{2 c}$$

$$P_n^{++} = -2 \sin(t/2) \sin(n+2)t \, / \, \cos(t/2) \tag{2 d}$$

$$P_n^{--} = 2 \cos(t/2) \sin(n+2)t \, / \, \sin(t/2) \tag{2 e}$$

$$P_n^{+-} = 2 \cos(n+2)t \tag{2 f}$$

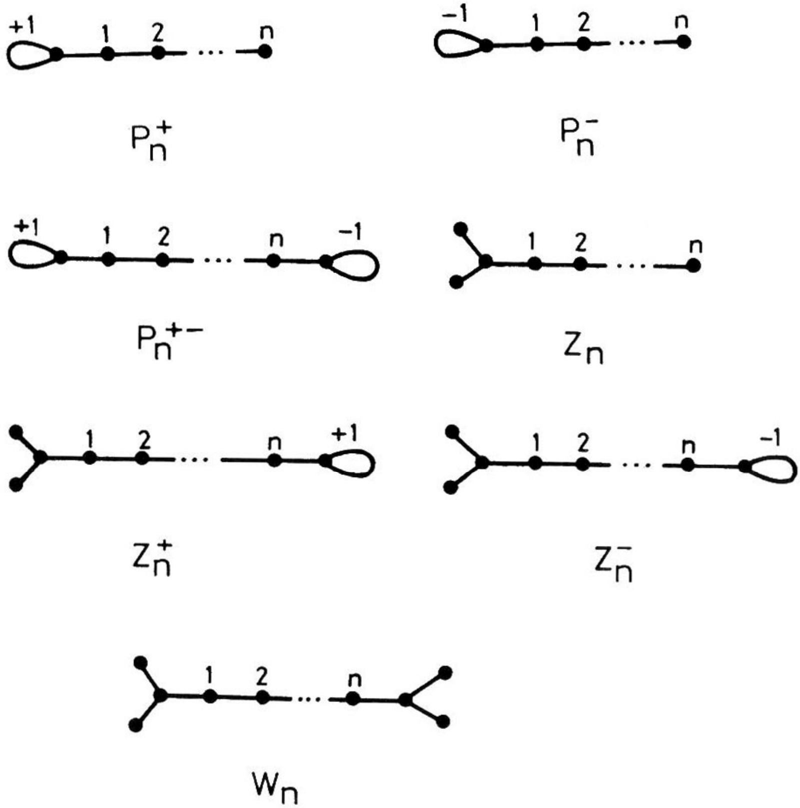
$$Z_n = 4 \cos t \cos(n+2)t \tag{2 g}$$

$$Z_n^+ = -8 \cos t \sin(t/2) \sin \frac{(2n+5)t}{2} \tag{2 h}$$

$$Z_n^- = 8 \cos t \cos(t/2) \cos \frac{(2n+5)t}{2} \tag{2 i}$$

$$W_n = -16 \sin t \cos^2 t \sin(n+3)t \tag{2 j}$$

with $x = 2 \cos t$ and the graphs P_n^+, P_n^-, P_n^{+-}, Z_n, Z_n^+, Z_n^- and W_n being given as follows.



Details on eqs. (2 a-j) can be found elsewhere[4], where also references to previous work on these polynomials are given. We offer five additional expressions of the same type, viz.,

$$P_n^{o} = 2\cos(n+2)t \tag{2 k}$$

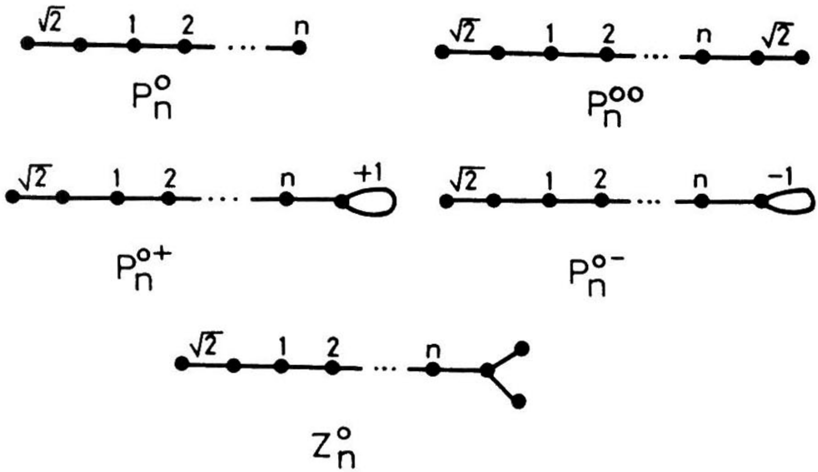
$$P_n^{oo} = -4 \sin t \sin(n+3)t \tag{2 l}$$

$$P_n^{o+} = -4 \sin(t/2) \sin \frac{(2n+5)t}{2} \tag{2 m}$$

$$P_n^{o-} = -4 \cos(t/2) \cos \frac{(2n+5)t}{2} \tag{2 n}$$

$$Z_n^{o} = -8 \cos t \sin t \sin(n+3)t \tag{2 o}$$

where again $x = 2\cos t$ and the graphs P_n^{o}, P_n^{oo}, P_n^{o+}, P_n^{o-} and Z_n^{o} are given as follows.



From eqs. (2) the zeros of the fifteen characteristic polynomials can be easily calculated and thus one obtains the spectra of the pertinent polymethine graphs. Therefrom we can evaluate various reactivity indices of the polymethines under consideration, since the pi-electron energy levels (as calculated within the Hückel molecular orbital model) coincide with the graph eigenvalues. These results, however, will not be given here in explicite form. We note also that the zeros of P_n^o were recently used by Herndon and Párkányi for calculation of the resonance energy of annulenes and their heteroderivatives.[5]

Another conclusion from eqs. (2) is that the spectra of the considered polymethine graphs are mutually strongly interrelated. For example, $P_n^{++} = (x - 2)\ P_{n+1}$, $P_n^{--} = (x + 2)\ P_{n+1}$, $P_n^{+-} = P_n^o$, $Z_n^+ = x\ P_n^{o+}$, $Z_n^- = x\ P_n^{o-}$, $Z_n^o = x\ P_n^{oo}$, $W_n = x^2\ (x^2 - 4)\ P_n$ etc.

Among the fifteen above mentioned polymethine graphs, only three: P_n, Z_n and W_n are simple, i.e. have no self-loops and/or weighted edges. In spite of considerable efforts and numerous attempts, no more simple polymethine graphs were found whose spectra can be expressed by means of analytical formulas. Therefore we must conclude that the finding of a fourth (simple) polymethine graph of this kind seems to be rather difficult and is maybe impossible. It should be a challenge for the colleagues to prove or disprove our previous conjecture[4] that P_n, Z_n and W_n are the only polymethine graphs, the spectra of which can be expressed in analytical form.

In order to deduce further consequences of eq. (1) we need the following result.

Lemma. Let $X_n = f\, X_{n-1} + g\, X_{n-2}$ and $Y_n = f\, Y_{n-1} + g\, Y_{n-2}$ be two recurrence relations with the coefficients f and g being independent of n. Let $R_{n,m} = X_n Y_m - X_{n+1} Y_{m-1}$. Then

$$R_{n,m} = (-g)^k R_{n-k,m-k} \qquad (3)$$

for all values of the integers n, m and k.

Proof. For $k = 0$ eq. (3) is automatically fulfilled. Suppose first that $k > 0$ and that the equation $R_{n,m} = (-g)^{k-1} R_{n-k+1,m-k+1}$ is true. Then

$$R_{n,m} = (-g)^{k-1} (X_{n-k+1} Y_{m-k+1} - X_{n-k+2} Y_{m-k}) =$$

$$= (-g)^{k-1} (X_{n-k+1}(f\, Y_{m-k} + g\, Y_{m-k-1}) - (f\, X_{n-k+1} +$$

$$+ g\, X_{n-k}) Y_{m-k}) = (-g)^{k-1} (g\, X_{n-k+1} Y_{m-k-1} -$$

$$- g X_{n-k} Y_{m-k}) = (-g)^k (X_{n-k} Y_{m-k} - X_{n-k+1} Y_{m-k-1}) =$$

$$= (-g)^k R_{n-k,m-k}$$

Therefore eq. (3) holds for all $k = 1,2,3,\ldots$. The proof in the case of negative k is analogous. Q.E.D.

Corollaries

$$G_n G_m - G_{n+1} G_{m-1} = G_{n-k} G_{m-k} - G_{n-k+1} G_{m-k-1}$$

$$G_n G_m - G_{n+1} G_{m+1} = G_{n-m+1} G_1 - G_{n-m+2} G_0$$

$$G_n^2 - G_{n+1} G_{n-1} = (G_1)^2 - G_2 G_0$$

$$P_n^2 - P_{n+1} P_{n-1} = 1$$

Let G be a graph with N vertices. Then we introduce a new graphic polynomial (G) as $(G) = x^N \left| G(-i/x) \right|$, where $i = \sqrt{-1}$. In terms of the polynomial (G), eq. (1) reads

$$(G_n) = x (G_{n-1}) + (G_{n-2})$$

while the Corollaries become

$$(G_n)(G_m) - (G_{n+1})(G_{m-1}) = (-1)^k \left((G_{n-k})(G_{m-k}) - \right.$$

$$\left. - (G_{n-k+1})(G_{m-k-1}) \right)$$

$$(G_n)(G_m) - (G_{n+1})(G_{m-1}) = (-1)^{m-1} \left((G_{n-m+1})(G_1) - \right.$$

$$\left. - (G_{n-m+2})(G_0) \right)$$

$$(G_n)^2 - (G_{n+1})(G_{n-1}) = (-1)^{n-1} ((G_1)^2 - (G_2)(G_0))$$

$$(P_n)^2 - (P_{n+1})(P_{n-1}) = (-1)^{n-1}$$

Some topological pi-electron properties of polymethines

According to the author's experience, the specific spectral properties of the polymethine graphs are (and must be) consequences of the recurrence relation (1). A number of these properties have been summarized in the preceding section.

Some of the mathematical results obtained, have particularly intriguing chemical implications. Before presenting a few of them, we would like to emphasize that the topological pi-electron characteristics of polymethines seem to be rather interesting and chemically non-trivial. Only a limited number of them are nowadays well understood and future investigations in this field are both necessary and promising.

Property 1.[1,2] In conjugated systems which are represented by the graphs P_n^{++} and P_n^{--} the bond orders between the atoms r and r+1 (r = 1,2,...,n-1) are all mutually equal.

Property 2.[6] If A is an arbitrary non-alternant and B an arbitrary alternant conjugated fragment, then the pi--electron charges alternate in sign along the polymethine chain of G_n, i.e. $q_r q_{r+1} < 0$ (r = 1,2,...,n-1).

Property 3.[7] If G_n is an arbitrary alternant polymethine, containing a single heteroatom in the position v_a of the fragment A, then the pi-electron charges alternate in sign along the polymethine chain of G_n, i.e. $q_r q_{r+1} < 0$ (r = 1,2,...,n-1).

It is to be noted that Properties 2 and 3 have been recently proved[6,7] by applying certain special cases of the Lemma.

We prove here another regularity in the pi-electron structure of polymethines, which is also based on our Lemma.

If G is alternant, then the atom-atom polarizability π_{rs} of the atoms r and s is given by the integral formula[7]

$$\pi_{rs} = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{(G-v_r)(G-v_s) - (G)(G-v_r-v_s)}{(G)^2} \, dx \qquad (4)$$

Property 4. Let G_n be an arbitrary alternant polymethine. Let v_r and v_s be atoms belonging to the polymethine chain of G_n $(r < s)$, whose distance is $d(r,s)$. Then

$$\text{sign } \pi_{rs}(G_n) = (-1)^{d(r,s)}$$

Proof. According to eq. (4), the sign of $\pi_{rs}(G_n)$ coincides with the sign of the expression $(G_n-v_r)(G_n-v_s) - (G_n)(G_n-v_r-v_s)$, provided it has the same sign for all values of the variable x.

Let first introduce two auxiliary polymethine graphs A_m and B_m.

A_m B_m

Then

$$(G_n - v_r) = (A_{r-1})(B_{n-r})$$

$$(G_n - v_s) = (A_{s-1})(B_{n-s})$$

$$(G_n - v_r - v_s) = (A_{r-1})(B_{n-s})(P_{s-r-1})$$

$$(G_n) = (A_r)(B_{n-r}) + (A_{r-1})(B_{n-r-1})$$

and consequently, $(G_n - v_r)(G_n - v_s) - (G_n)(G_n - v_r - v_s) =$
$= (A_{r-1})(B_{n-s})(\ (B_{n-r})(A_{s-1}) - (A_r)(B_{n-r})(P_{s-r-1}) -$
$- (A_{r-1})(B_{n-r-1})(P_{s-r-1})\ ) = (A_{r-1})(B_{n-s})(\ (A_{r-1})(B_{n-r})$
$(P_{s-r-2}) - (A_{r-1})(B_{n-r-1})(P_{s-r-1})\ )$ because of
$(A_r)(P_{s-r-1}) = (A_{s-1}) - (A_{r-1})(P_{s-r-2})$. Further we have
$(G_n - v_r)(G_n - v_s) - (G_n)(G_n - v_r - v_s) = (A_{r-1})^2\ (B_{n-s})$
$(\ (B_{n-r})(P_{s-r-2}) - (B_{n-r-1})(P_{s-r-1})\ ) = (A_{r-1})^2\ (B_{n-s})$
$(-1)^k\ (\ (B_{n-r-k})(P_{s-r-k-2}) - (B_{n-r-k-1})(P_{s-r-k-1})\ )$
because of the Lemma. For $k = s - r - 1$ we finally gain

$$(G_n - v_r)(G_n - v_s) - (G_n)(G_n - v_r - v_s) = (-1)^{s-r}\ (A_{r-1})^2\ (B_{n-s})^2$$

Statement 4 follows now from eq. (4) and the fact that $d(r,s) = s - r$. Q.E.D.

Some additional topological pi-electron properties of polymethines can be found elsewhere.[7,8]

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