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Original Investigations

Topological Studies on Heteroconjugated Molecules

Alternant Systems with One Heteroatom

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A graph-theoretical analysis of certain π-electron properties of alternant molecules with one heteroatom is given. Topological formulas for total π-electron energy, π-electron charge density, bond order and various polarizabilities are derived. The main results of the paper are summarized in Rules 1–7.

Key words: Graph theory – Heteroconjugated molecules

1. Introduction

In recent years graph-theoretical methods were frequently applied in theoretical investigations of conjugated molecules [1]. The success of this "topological" approach to conjugated compounds is based mainly on a close relation between the Hamiltonian matrix in the Hückel molecular orbital (HMO) theory and the adjacency matrix of the so called "molecular graph" [2]. Many of the previous investigations in this field deal with conjugated hydrocarbons, and the topological properties of these compounds are nowadays well understood [1]. This is a proper consequence of the fact that only the molecular graphs of hydrocarbons are simple graphs (i.e. possess no self-loops and weighted edges).

It is natural to pose the question of the extension of the graph-theoretical approach also to heteroconjugated molecules. The present work offers some contributions in this direction. However, only the simplest class of such systems is considered, namely alternant molecules with one heteroatom. As it will be seen, the graph-theoretical analysis of these latter systems is much more complicated than the same treatment of alternant hydrocarbons. Analogous consideration of non-alternant heteroconjugated systems and molecules with several heteroatoms results in rather complex mathematical expressions, which can hardly provide any chemically relevant information.

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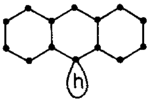
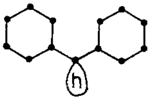
Preliminary topological results on alternant molecules with one heteroatom were reported in [3].

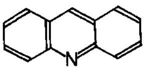
The way in which a heteroconjugated molecule is represented by a graph is described in detail elsewhere [3, 4]. For example, G_1^h and G_2^h are the molecular graphs of acridine (I) and diphenylamine (II), respectively.



G_1^h



G_2^h



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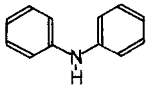

II

The position of the heteroatom is indicated by a self-loop of weight h on the corresponding vertex of the molecular graph G^h[1]. If $h \to 0$, the self-loop in G^h disappears and thus G^0 becomes the molecular graph of a conjugated hydrocarbon. Consequently, by setting $h=0$, all expressions which are obtained in the present work reduce to formulas valid for alternant hydrocarbons.

The necessary first step in the application of graphs to the molecular orbital theory of conjugated systems is the use of the Sachs theorem [5, 6]. This result, namely, relates the HMO secular polynomial with the structure of the molecular graph. The paper of Sachs [5] contains the explicit formulation of this theorem for simple graphs, together with an immediate (but implicitly given) generalization for graphs with self-loops and/or weighted edges. In recent chemical literature the generalized Sachs formula was published by various authors [4, 7].

In the present paper we offer a topological analysis of the three most important π-electron indices of conjugated systems – total π-electron energy, charge density distribution and bond order. For this purpose we need a number of graph-theoretical definitions. These are explained in the subsequent section, together with the adopted notation and terminology.

2. Graph-Theoretical Representation of Alternant Molecules with One Heteroatom

We shall consider molecular graphs with N vertices. The unique self-loop is located on the vertex r. If the weight of this self-loop is h, we shall denote the corresponding molecular graph by G^h. The adjacency matrix A^h and the char-

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[1] We consider molecular graphs without weighted edges. This is equivalent to the approximation $\beta_{CX}=\beta_{CC}$ in the HMO theory.

acteristic polynomial $P(G^h, x)$ of the graph G^h are defined as usual [4, 6, 7]

$$(A^h)_{uv} = \begin{cases} h & \text{if } u=v=r \\ 1 & \text{if the vertices } u \text{ and } v \text{ are adjacent} \\ 0 & \text{otherwise} \end{cases}$$

$$P(G^h, x) = \det (xI - A^h)$$

If $h=0$, then we denote the molecular graph simply by G. Hence, G contains no self-loop and represents the parent hydrocarbon of the heteroconjugated system

The subgraph $G\text{–}u$ is obtained by deletion of the vertex u from G. Thus $G\text{–}u$ contains $N\text{–}1$ vertices. The subgraph $G\text{–}uv$, which possesses $N\text{–}2$ vertices, is obtained by deletion of the vertices u and v from G. The subgraph $G\text{–}uvz$ is defined analogously.

In order to write the expressions which follow in a more dense form, we introduce the function (G) as

$$(G) = i^{-N} P(G, ix) \tag{1}$$

where i is the imaginary unit. The polynomial $(G\text{–}u)$ is given accordingly by

$$(G\text{–}u) = i^{-N+1} P(G\text{–}u, ix) \tag{2}$$

If G^h is alternant, then evidently G and $G\text{–}r$ are alternant too. Because of the pairing theorem, one can write their characteristic polynomials in the form [1]

$$P(G, x) = \sum_j (-1)^j a_j x^{N-2j}$$

$$P(G\text{–}r, x) = \sum_j (-1)^j b_j x^{N-1-2j}$$

In the above notation, the coefficients of $P(G, x)$ and $P(G\text{–}r, x)$ are written in such a manner that $a_j \geqslant 0$ and $b_j \geqslant 0$. Then (G) and $(G\text{–}r)$ are polynomials with real, non-negative coefficients, namely

$$(G) = \sum_j a_j x^{N-2j}; \qquad (G\text{–}r) = \sum_j b_j x^{N-1-2j}$$

(G) is either an even or an odd function, depending on whether N is even or odd. The parity of the function $(G\text{–}r)$ is, of course, opposite to that of (G).

We introduce now an important topological function $V_r = V_r(x)$ as

$$V_r = (G\text{–}r)/(G) \tag{3}$$

Another function of this type, V_{rs}, is defined analogously by

$$V_{rs} = (G\text{–}rs)/(G) \tag{4}$$

It is easy to show that $V_r(x)$ has the following behaviour for small and large values of x.

$$V_r \sim \begin{cases} x b_{k-1}/a_k & \text{if } x \to 0 \text{ and } N=2k \\ b_k/(x a_k) & \text{if } x \to 0 \text{ and } N=2k+1 \end{cases} \tag{5}$$

$$V_r \sim 1/x \qquad \text{if } x \to \infty \tag{6}$$

According to the (generalized) Sachs theorem [4, 5, 7], it is

$$P(G^h, x) = P(G, x) - hP(G\text{–}r, x)$$

which combined with Eqs. (1) and (2) gives

$$(G^h) = (G) + ih(G\text{–}r) \tag{7}$$

Further graph-theoretical definitions will be introduced where necessary.

3. Total π-Electron Energy of Alternant Molecules with One Heteroatom

In order to simplify the mathematical formulas in this and the following sections, the abbreviate notation

$$\frac{1}{\pi} \int_{-\infty}^{+\infty} F(x)\, dx \equiv \langle F(x) \rangle \equiv \langle F \rangle$$

will be used for a frequently occurring type of integrals. Then the Coulson formula for total π-electron energy differences reads [8, 3]

$$E^h - E = h + \langle \ln |(G^h)/(G)| \rangle$$

where E^h and E are the total π-electron energy of G^h and G, respectively. Taking into account Eq. (7) and the fact that G^h is alternant, one obtains [3]

$$E^h - E = h + \tfrac{1}{2} \langle \ln (1 + h^2 V_r^2) \rangle \tag{8}$$

with V_r being defined by Eq. (3). An important conclusion which can be immediately drawn from Eq. (8) is $E^h - E - h > 0$, which is interpreted by the following rule [3]. The rule is valid for alternant systems possessing a heteroatom being more electronegative than carbon (i.e. $h > 0$).

Rule 1. A heteroconjugated molecule is always more stable than its parent hydrocarbon.

Series expansion of the integral in Eq. (8) gives

$$E^h - E = h + \tfrac{1}{2} h^2 \langle V_r^2 \rangle - \tfrac{1}{4} h^4 \langle V_r^4 \rangle + \cdots \tag{9}$$

showing that the self-polarizability of the site r is

$$\pi_{rr} = \langle V_r^2 \rangle \tag{10}$$

From (9) is seen that $E^h > E + h + \frac{1}{2} h^2 \pi_{rr}$, provided, of course, that $h > 0$.

Rule 2a. Second order perturbation theory necessarily underestimates the value of E^h. Similarly, third order perturbation theory will overestimate E^h, etc.

A method for approximate evaluation of the integral in Eq. (8) has been developed in Refs. [3, 9]. The method is based on the knowledge of the asymptotic behaviour of the integrand for $x \to 0$ and $x \to \infty$. Because of the relations (5) and (6) we have

$$V_r^2 \approx \frac{b_{k-1}^2 x^2}{(a_k + b_{k-1} x^2)^2} \quad \text{for } N = 2k$$

$$V_r^2 \approx \frac{b_k^2 + x^2}{(a_k^2 + x^2) x^2} \quad \text{for } N = 2k+1$$

Substitution of these latter approximations back into Eq. (8) yields after straightforward integration

$$E^h \doteq E + h + (h^2 + 4a_k/b_{k-1})^{1/2} - (4a_k/b_{k-1})^{1/2} \tag{11}$$

for $N = 2k$, and

$$E^h \doteq E + h + (h^2 + 2|h| b_k + a_k^2)^{1/2} - a_k$$

for $N = 2k+1$.

The coefficients a and b in the above approximate formulas have the following well known topological interpretation [10].

$$a_k = [\mathrm{ASC}(G)]^2; \qquad b_{k-1} = \sum_u [\mathrm{ASC}(G\text{–}ru)]^2 \quad \text{for } N = 2k$$

$$a_k = \sum_u [\mathrm{ASC}(G\text{–}u)]^2; \qquad b_k = [\mathrm{ASC}(G\text{–}r)]^2 \quad \text{for } N = 2k+1$$

Here ASC denotes the algebraic structure count of the corresponding molecular graph [1, 11]. It is worth mentioning that $(4a_k/b_{k-1})^{1/2}$ in Eq. (11) is equal to the Dewar index D_r of the site r of the parent hydrocarbon [10, 12]. Hence, Eq. (11) is rewritten as

$$E^h \doteq E + h + (h^2 + D_r^2)^{1/2} - D_r$$

and a general rule follows for molecules with even number of conjugated centers (i.e. $N = 2k$).

Rule 3. The stability of a heteroconjugated molecule is a decreasing function of the Dewar index of the site where the heteroatom is located. Among positional isomers with one heteroatom, the most (least) stable one is that with the heteroatom in position with minimal (maximal) Dewar index.

4. Charge Density Distribution and Bond Orders in Alternant Molecules with One Heteroatom

The introduction of a heteroatom into an alternant conjugated hydrocarbon results in non-uniform π-electron charge distribution. Many years ago Coulson and Longuet-Higgins [13] noticed the alternation of positive and negative charges along a carbon atom chain in heteroconjugated molecules. Little has been done thereafter on the elucidation of this remarkable topological phenomenon.

According to the classical results of Coulson and Longuet-Higgins [14], the π-electron charge density on the conjugated center s is given by

$$q_s^h = 1 - \langle P(G^h\text{–}s, ix)/P(G^h, ix)\rangle$$

or in another notation

$$q_s^h = 1 + i\langle (G^h\text{–}s)/(G^h)\rangle \tag{12}$$

Substitution of the recurrence relations (7) and (13)

$$(G^h\text{–}s) = (G\text{–}s) + ih(G\text{–}rs) \tag{13}$$

into Eq. (12) yields

$$q_s^h = 1 + h\left\langle \frac{(G\text{–}r)(G\text{–}s) - (G)(G\text{–}rs)}{(G)^2 + h^2(G\text{–}r)^2} \right\rangle + i\left\langle \frac{(G)(G\text{–}s) + h^2(G\text{–}r)(G\text{–}rs)}{(G)^2 + h^2(G\text{–}r)^2} \right\rangle \tag{14}$$

In the present work it is assumed that G^h is alternant. Therefore both the products $(G)(G\text{–}s)$ and $(G\text{–}r)(G\text{–}rs)$ are odd functions and the second integral in formula (14) vanishes. Thus for alternant systems we get

$$q_s^h = 1 + h\left\langle \frac{(G\text{–}r)(G\text{–}s) - (G)(G\text{–}rs)}{(G)^2 + h^2(G\text{–}r)^2} \right\rangle \tag{15}$$

This topological formula is also written in the form

$$q_s^h - q_s = h\left\langle \frac{(G\text{–}r)(G\text{–}s) - (G)(G\text{–}rs)}{(G)^2 + h^2(G\text{–}r)^2} \right\rangle \tag{16}$$

because in alternant hydrocarbons the charge distribution is uniform (i.e. all $q_s = 1$).

From Eq. (15) is seen that the charge density on the site s is almost linearly proportional to the weight h of the self-loop on the vertex r, but depends also on a delicate balance of two very similar topological functions $(G\text{–}r)(G\text{–}s)$ and $(G)(G\text{–}rs)$. Therefore the prediction of the sign of the π-electron charge on the basis of topological arguments seems to be a rather difficult task in the general case. In the next section a special situation is discussed, where a considerable simplification of Eq. (15) occurs.

Series expansion of Eq. (15) gives

$$q_s^h = 1 + h\langle V_r V_s - V_{rs}\rangle - h^3\langle (V_r V_s - V_{rs}) V_r^2\rangle + \cdots \tag{17}$$

from which a topological formula for atom-atom polarizability π_{rs} is seen to be

$$\pi_{rs} = \langle V_r V_s - V_{rs} \rangle \tag{18}$$

The V-functions are given by Eqs. (3) and (4).

Rule 4. The expressions $q_s^h - 1$ and $h\pi_{rs}$ have equal sign. Hence the sign of the π-electron charges in alternant molecules with one heteroatom is always correctly predicted by means of atom-atom polarizability.

From Eq. (17) it can be also concluded that $q_s^h < 1 + h\pi_{rs}$ if $h\pi_{rs} > 0$ and $q_s^h > 1 + h\pi_{rs}$ if $h\pi_{rs} < 0$. Hence, in all cases $|1 - q_s^h| < |h\pi_{rs}|$.

Rule 2b. First order perturbation theory (i.e. the use of atom-atom polarizabilities) overestimates the absolute value of the π-electron charges in alternant molecules with one heteroatom. In the same way second-order perturbation theory will underestimate q_s^h etc.

For $r = s$ the subgraph G–rs is not defined. It is consistent, however, to set $(G\text{–}rr) \equiv 0$. Then Eq. (15) becomes

$$q_r^h = 1 + h \left\langle \frac{(G\text{–}r)^2}{(G)^2 + h^2 (G\text{–}r)^2} \right\rangle$$

while (18) reduces to Eq. (10).

The graph-theoretical expression for bond order in an alternant molecule with one heteroatom is derived by a procedure analogous to that used in Ref. [15]. Since it requires rather tedious algebraic manipulations, we present here only the final formula, valid for adjacent vertices s and t.

$$p_{st}^h = \left\langle \frac{(G)(G\text{–}st) + h^2 (G\text{–}r)(G\text{–}rst)}{(G)^2 + h^2 (G\text{–}r)^2} \right\rangle + \\ + \sum_Z (-1)^{z/2-1} \left\langle \frac{(G)(G\text{–}Z) + h^2 (G\text{–}r)(G\text{–}r\text{–}Z)}{(G)^2 + h^2 (G\text{–}r)^2} \right\rangle \tag{19}$$

In the above expression Z denotes a cycle of the length z. The summation goes over all cycles of G which contain the bond st. The subgraphs G–Z and G–r–Z are obtained by deletion of Z from G and G–r, respectively [15]. If Z contains the vertex r, then G–r–Z is not defined and it is to be assumed that $(G\text{–}r\text{–}Z) \equiv 0$. Similarly, it is $(G\text{–}rst) \equiv 0$ if $r = s$ or $r = t$.

By setting $h = 0$ we obtain from Eq. (19) the previously known [15] formula for bond order in alternant hydrocarbons.

$$p_{st} = \left\langle \frac{(G\text{–}st)}{(G)} \right\rangle + \sum_Z (-1)^{z/2-1} \left\langle \frac{(G\text{–}Z)}{(G)} \right\rangle$$

This enables one to write Eq. (19) in the form

$$p_{st}^h - p_{st} = h^2 \left\langle \frac{(G\text{–}r)[(G)(G\text{–}rst) - (G\text{–}r)(G\text{–}st)]}{(G)[(G)^2 + h^2 (G\text{–}r)^2]} \right\rangle + \\ + h^2 \sum_Z (-1)^{z/2-1} \left\langle \frac{(G\text{–}r)[(G)(G\text{–}r\text{–}Z) - (G\text{–}r)(G\text{–}Z)]}{(G)[(G)^2 + h^2 (G\text{–}r)^2]} \right\rangle \tag{20}$$

There exists a deep and intriguing analogy between Eqs. (16) and (20). Thus the introduction of a heteroatom in a conjugated hydrocarbon causes changes in bond orders (and therefore also in bond lengths), which are almost linearly proportional to h^2. In the general case, however, it is difficult to predict whether a bond st will be lengthened or shortened, because the sign of $p^h_{st} - p_{st}$ depends on the differences of closely related topological expressions $(G)(G\text{–}rst)$ and $(G\text{–}r)(G\text{–}st)$ etc. In the next section we shall be able to say more about $p^h_{st} - p_{st}$ for a special class of conjugated systems.

Since the bond order p^h_{st} depends on h^2, it is $d(p^h_{st})/dh = 0$ for $h = 0$. This is equivalent to the well known finding that the bond-atom polarizability $\pi_{st,r}$ vanishes for all sites r and bonds st in arbitrary alternant hydrocarbons.

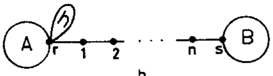
In the case when the bond st does not belong to any cycle (e.g. such are all bonds in acyclic molecules), Eqs. (19) and (20) reduce to

$$p^h_{st} = \left\langle \frac{(G)(G\text{–}st) + h^2(G\text{–}r)(G\text{–}rst)}{(G)^2 + h^2(G\text{–}r)^2} \right\rangle =$$

$$= p_{st} + h^2 \left\langle \frac{(G\text{–}r)[(G)(G\text{–}rst) - (G\text{–}r)(G\text{–}st)]}{(G)[(G)^2 + h^2(G\text{–}r)^2]} \right\rangle \qquad (21)$$

5. Three Theorems for Charge Distribution and Bond Order

In the present section we shall study a class of heteroconjugated molecules in which the site s is separated from the heteroatom (at position r) by a linear polyene chain of n carbon atoms ($n = 0, 1, 2, \ldots$). Such systems are represented by graphs of the form G^h_n.



G^h_n

The subgraphs A and B symbolize arbitrary alternant fragments of the molecule.

It is worth mentioning that the graphs of the type G^h_n were subject of various recent theoretical investigations [16, 17]. The graphs G_n (these are the graphs G^h_n for $h = 0$) fulfil the identities [17, 18]

$$(G_n) = (A)(B)(P_n) + [(A)(B\text{–}s) + (A\text{–}r)(B)](P_{n-1}) + (A\text{–}r)(B\text{–}s)(P_{n-2}) \qquad (22a)$$

$$(G_n\text{–}r) = (A\text{–}r)[(B)(P_n) + (B\text{–}s)(P_{n-1})] \qquad (22b)$$

$$(G_n\text{–}s) = (B\text{–}s)[(A)(P_n) + (A\text{–}r)(P_{n-1})] \qquad (22c)$$

$$(G_n-rs)=(A-r)(B-s)(P_n) \tag{22d}$$

$$(G_n-ns)=(B-s)[(A)(P_{n-1})+(A-r)(P_{n-2})] \tag{22e}$$

$$(G_n-rns)=(A-r)(B-s)(P_{n-1}) \tag{22f}$$

where P_n is the path (= linear chain) with n vertices. From Eqs. (22) it follows

$$(G_n-r)(G_n-s)-(G_n)(G_n-rs)=(A-r)^2(B-s)^2[(P_{n-1})^2-(P_n)(P_{n-2})] \tag{23}$$

$$(G_n)(G_n-rns)-(G_n-r)(G_n-ns)=(A-r)^2(B)(B-s)[(P_{n-1})^2-(P_n)(P_{n-2})] \tag{24}$$

In the Appendix it is proved that

$$(P_{n-1})^2-(P_n)(P_{n-2})=(-1)^{n+1} \tag{25}$$

Combining Eqs. (23) and (25) with Eq. (15), one obtains

$$q_s^h=1+(-1)^{n+1}h\left\langle\frac{(A-r)^2(B-s)^2}{(G_n)^2+h^2(G_n-r)^2}\right\rangle \tag{26}$$

The integral on the right side of Eq. (26) is evidently positive and one deduces the following important conclusion, valid for heteroconjugated systems G_n^h.

Rule 5 (*The Charge Alternation Rule*). The charge on the atom s is positive (negative) if the distance between s and the heteroatom is odd (even).

In the formulation of the above theorem it is assumed that the heteroatom is more electronegative than carbon ($h>0$). For the case of negative h, Rule 5 is to be modified accordingly. Of course, the distance between the atoms r and s is $n+1$ in our notation.

For the bond order of the bond ns, Eq. (21) applies. Then substitution of (24) and (25) back into (21) gives

$$p_{ns}^h-p_{ns}=(-1)^{n+1}h^2\left\langle\frac{(G_n-r)(A-r)^2(B)(B-s)}{(G_n)[(G_n)^2+h^2(G_n-r)^2]}\right\rangle \tag{27}$$

Rule 6 (*The Bond Order Alternation Rule*). The introduction of a heteroatom decreases (increases) the bond order of the bonds with an odd (even) distance from the heteroatom.

The above rule is valid for heteroatoms with both positive and negative values of h. The distance of the bond ns from the heteroatom is $n+1$ in our notation.

From the identity [18] $(P_n)=x(P_{n-1})+(P_{n-2})$ it is seen that the coefficients of the polynomial (P_n) rapidly increase with increasing n. From Eqs. (22) it is then evident that also (G_n) and (G_n-r) have a similar dependence on n. Since the expressions $(A-r)^2(B-s)^2$ and $(A-r)^2(B)(B-s)$ are completely independent of n, the integrals in Eqs. (26) and (27) must be rapidly decreasing functions of the length of the linear polyene fragment. Therefore we deduce the following rules.

Rule 7a. The absolute value of the π-electron charge rapidly decreases when the distance from the heteroatom increases.

Rule 7b. The effect of a heteroatom on bond order rapidly decreases when the distance of the bond from the heteroatom increases.

Although the three rules in this section are proved only for a relatively narrow class of heteroconjugated molecules, we expect that the range of validity of these results is much wider.

Appendix

In order to prove Eq. (25), we shall demonstrate the validity of a more general statement (28). For an arbitrary system G_n containing a linear polyene fragment of length n, the following recurrence relation holds [17].

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

Therefrom one gets

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

This identity shows that the polynomial $(-1)^{n+1}[(G_{n-1})^2-(G_n)(G_{n-2})]$ is independent of n and therefore

$$(G_{n-1})^2-(G_n)(G_{n-2})=(-1)^n[(G_1)^2-(G_2)(G_0)]. \qquad (28)$$

If we set $G_n=P_n$, we obtain Eq. (25) as a special case of (28), because of

$$(P_2)=x^2+1,\ (P_1)=x,\ (P_0)=1.$$

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