Topological Studies on Heteroconjugated Molecules. III. On the Law of Alternating Polarity

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The π-electron charge Q_s^h in alternant conjugated systems with one heteroatom is considered. A complete proof of the law of alternating polarity is presented. The integral expression for Q_s^h is decomposed into a number of relatively simple terms, which give some insight into the dependence of Q_s^h on molecular topology.

The law of alternating polarity is one of the classic results in Hückel molecular orbital theory (see e.g. [1]). It was formulated and proved by Coulson and Longuet-Higgins [2]. According to this law, in an alternant conjugated π-electron system with one heteroatom, two adjacent atoms have always opposite polarity, i.e. their π-electron charges have opposite signs. In other words, the π-electron charges alternate in sign along any path in an alternant conjugated system with one heteroatom.

In fact, Coulson and Longuet-Higgins [2] demonstrated only the sign alternation of the atom-atom polarizabilities in alternant hydrocarbons, although (as we shall see here) a quite similar argument can be used also in the case of π-electron charges.

In the present paper some results related to the law of alternating polarity will be exposed, which are obtained from graph theoretical considerations. A graph representation of heteroconjugated systems was developed in the first two parts of this series [3, 4] and elsewhere [5].

We shall use the same notation as in [4]. Thus G^h is the molecular graph corresponding to a heteroconjugated system with the (single) heteroatom in the position r. By G we denote the molecular graph of the parent hydrocarbon.

In [4] it is shown that if G^h is alternant, then the π-electron charge Q_s^h on the atom s is given by

$$Q_s^h = -h\left\langle \frac{(G-r)(G-s)-(G)(G-rs)}{(G)^2+h^2(G-r)^2} \right\rangle, \tag{1}$$

whereas the atom-atom polarizability π_{rs} conforms to the relation

$$\pi_{rs} = \left\langle \frac{(G-r)(G-s)-(G)(G-rs)}{(G)^2} \right\rangle. \tag{2}$$

The π-electron charge density q_s^h is, of course, related with Q_s^h as $q_s^h = 1 - Q_s^h$.

If H denotes a graph with n vertices, then in the above formulae (H) symbolizes the polynomial (in the variable x) which is related to the characteristic polynomial $P(H, x)$ of H as follows:

$$(H) = i^{-n} P(H, ix).$$

For the present work it is important to note [4] that if H is a bipartite graph, then (H) is a polynomial with real, non-negative coefficients. Therefore $(H) > 0$ for all positive values of the variable x. (H) is an even (odd) function of x if n is even (odd). All graphs considered in this paper are bipartite.

The vertices of a bipartite graph can be partitioned into two classes, such that no two vertices belonging to the same class are adjacent.

A path in the graph G is a sequence of mutually distinct vertices $v_0, v_1, \ldots, v_p$, such that v_{i-1} is adjacent to v_i, $i = 1, 2, \ldots, p$. Such a path is said to be of length p, and to connect the vertices v_0 and v_p.

Let r and s be two fixed vertices of G. Then W will denote a path connecting r and s; the length of W is w. In the general case the vertices r and s are connected by several paths. The length of the shortest path is the distance between r and s and will be denoted by d(r, s).

If G is a connected bipartite graph, then d(r, s) is even if the vertices r and s belong to the same class and odd if they belong to different classes.

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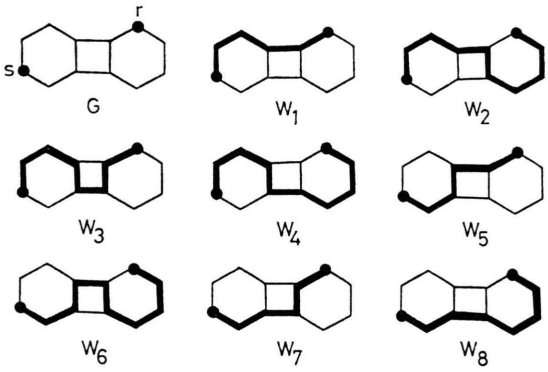
For example, there are eight different paths W_1–W_8 connecting the vertices r and s of the molecular graph of biphenylene. Since r and s belong to different classes, the length of all these paths is odd.



Following the notation of Coulson and Longuet-Higgins [6] we shall write

$$\Delta = \det(\boldsymbol{A} - x\boldsymbol{I}),$$

where $\boldsymbol{A}$ is the adjacency matrix of G, and $\boldsymbol{I}$ the unit matrix of order N. Of course,

$$\Delta = (-1)^N \det(x\boldsymbol{I} - \boldsymbol{A}) = (-1)^N P(G, x).$$

Let in addition $\Delta_{\mathrm{ab}\ldots,\mathrm{fg}\ldots}$ mean that the rows a, b, ... together with the columns f, g, ... have been removed from the determinant Δ. Then, by setting t = r and u = s in (56) of [6], we get

$$\Delta_{r,r}\Delta_{\mathrm{s,s}} - \Delta\,\Delta_{r\mathrm{s},r\mathrm{s}} = (\Delta_{r,\mathrm{s}})^2 \tag{3}$$

whereas by (78) of [6]

$$\Delta_{r,\mathrm{s}} = (-1)^{r+s}\sum_W (-1)^w \Delta_{v_0v_1\ldots v_p,\,v_0v_1\ldots v_p}, \tag{4}$$

with $v_0 = r$, $v_p = s$ and the summation going over all the paths W connecting r and s. Since

$$\begin{aligned} \Delta_{r,r} &= (-1)^{N-1}P(G-r),\\ \Delta_{\mathrm{s,s}} &= (-1)^{N-1}P(G-s),\\ \Delta_{r\mathrm{s},r\mathrm{s}} &= (-1)^{N-2}P(G-rs),\\ \Delta_{v_0v_1\ldots v_p,\,v_0v_1\ldots v_p} &= (-1)^{N-w-1}P(G-W), \end{aligned}$$

we arrive at the graph theoretical identity

$$P(G-r)\,P(G-s) - P(G)\,P(G-rs) = \Big[\sum_W P(G-W)\Big]^2. \tag{5}$$

(5) is an immediate graph theoretic reinterpretation of (3) and (4). Nevertheless, this result seems to have been fully overlooked until now both in graph spectral theory (e.g. [7]) and in the topological theory of conjugated molecules (e.g. [8]).

From (5) we straightforwardly obtain

$$(G-r)(G-s) - (G)(G-rs) = \Big[\sum_W i^w (G-W)\Big]^2. \tag{6}$$

Now, two cases are to be distinguished. If the vertices r and s belong to the same class (or if r = s), then all paths between them have even length. Thus i^w is real for all paths W. Consequently, $\sum_W i^w (G-W)$ is real and its square is positive for all (real) values of the variable x ($x \neq 0$). If, on the other hand, the vertices r and s belong to different classes, then all paths between them have odd length and therefore $\sum_W i^w (G-W)$ is purely imaginary and its square is positive for all (real) values of x ($x \neq 0$). Thus we have proved that

$$(-1)^{d(\mathrm{r,s})} \cdot [(G-r)(G-s) - (G)(G-rs)] \geqq 0 \tag{7}$$

for all x. The equality in (7) is fulfilled only for $x = 0$.

Combining the above inequality with (2), we obtain

Theorem 1 [2]. The atom-atom polarizabilities in an alternant hydrocarbon alternate in sign along any path in the molecule and

$$\operatorname{sign}\pi_{r\mathrm{s}} = (-1)^{d(\mathrm{r,s})}.$$

From (7) and (1) we conclude in a completely analogous manner that the following statement holds.

Theorem 2. The π-electron charges in an alternant conjugated system with one heteroatom alternate in sign along any path in the molecule and

$$\operatorname{sign} Q_{\mathrm{s}}^{\mathrm{h}} = -(-1)^{d(\mathrm{r,s})}\operatorname{sign} h.$$

This is just another formulation of the law of alternating polarity.

Substituting (6) back into (1) we deduce

Theorem 3.

$$Q_{\mathrm{s}}^{\mathrm{h}} = \sum_W Q_{\mathrm{s}}(W) + \sum_{\substack{W_\mathrm{a}\\ \mathrm{a}>\mathrm{b}}}\sum_{W_\mathrm{b}} Q_{\mathrm{s}}(W_\mathrm{a}, W_\mathrm{b}), \tag{8}$$

where

$$Q_{\mathrm{s}}(W) = Q_{\mathrm{s}}(W, W) = -h(-1)^{d(\mathrm{r,s})} \cdot \left\langle \frac{(G-W)^2}{(G)^2 + h^2(G-r)^2} \right\rangle \tag{9}$$

and

$$Q_{\mathrm{s}}(W_\mathrm{a}, W_\mathrm{b}) = -2h\, i^{w_\mathrm{a}+w_\mathrm{b}} \cdot \left\langle \frac{(G-W_\mathrm{a})(G-W_\mathrm{b})}{(G)^2 + h^2(G-r)^2} \right\rangle. \tag{10}$$

The above (exact) formula enables the following topological interpretation. The π-electron on the atom s is induced by the heteroatom in the position r. The influence of the heteroatom is transmitted by all paths W which connect r and s. The effect transmitted by the path W is $Q_s(W)$, the first summation in (8). The influence of the heteroatom is also simultaneously transmitted by two paths; their joint effects to the net charge on the atom s are given by the expressions $Q_s(W_a, W_b)$, second summation in (8). From the formulae (9) and (10) we can now deduce the following topological rules.

Rule 1. Let W be an arbitrary path of G, connecting r and s. The fraction of the total charge which is induced on the atom s by means of W is positive if $-(-1)^{d(r,s)}\, h > 0$ and negative if $-(-1)^{d(r,s)}\, h < 0$. Thus, not only the total effect of all paths, but also the effect of every individual path obeys the law of alternating polarity (Theorem 2).

The fraction of the total charge which is induced by means of pairs of paths may only change the magnitude, but not the sign of Q_s^h.

Rule 2. Let W_a and W_b be two distinct (but arbitrary) paths of G, connecting r and s. If $w_a (\mathrm{mod}\ 4) \equiv w_b (\mathrm{mod}\ 4)$, i.e. if the difference of the lengths of W_a and W_b is divisible by 4, then the effect of the pair W_a, W_b is "in phase" with the effect of individual paths and increases the magnitude of Q_s^h. In the opposite case the pair W_a, W_b has an "out of phase" effect, which decreases the magnitude of Q_s^h.

Regularities completely analogous to Theorem 2 and Rules 1 and 2 can be, of course, formulated also for atom-atom polarizability.

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