Topological Studies on Heteroconjugated Molecules. VI. Alternant Systems with Two Heteroatoms

Ivan Gutman
Vanderbilt University, Nashville, Tennessee, USA

Z. Naturforsch. **45a,** 1085–1089 (1990); received March 17, 1990

The collective effects of two heteroatoms on the total π-electron energy, resonance energy and charge distribution of alternant conjugated molecules are examined. Three general rules for the signs of these effects are formulated. All these rules are shown to have a common origin and are consequences of certain mathematical properties of graph propagators.

In our previous investigations of the topological properties of heteroconjugated molecules [1–5] we have been mainly concerned with the effects caused by a single heteroatom. Exceptionally, in [5] we studied the effect of two heteroatoms, whose electronegativities relative to sp^2-carbon are equal in magnitude and opposite in sign.

From first glance, heteroconjugated molecules with more than one heteroatom are not worth additional consideration because the total effect of the heteroatoms is expected to be simply the superposition of individual effects. We intend to demonstrate in this paper that such a viewpoint needs to be slightly modified. The sum of the individual effects differs from the total effect by a certain amount which we interprete as the result of a collective (i.e. simultaneous) influence of several heteroatoms.

The reason for communicating these results now (a good nine years after they were actually obtained) is the appearance of the book [6] in which the concept of graph propagators has been introduced. As will become evident later on, literally all results on heteroconjugated systems with two heteroatoms outlined in the present paper are connected with graph propagators and are consequences of certain mathematical properties thereof.

Relevant details of the MO theory of heteroconjugated molecules can be found in the book [7].

Notation

We shall mainly use the same notation and terminology as in [3]. Thus the parent hydrocarbon of the heteroconjugated system considered is represented by a graph G. Since we examine alternant conjugated systems, G is assumed to be bipartite. The number of vertices of G is denoted by n whereas $\phi(G, x) = \phi(G)$ stands for the respective characteristic polynomial. (Note that in [3] the characteristic polynomial was denoted by P.)

The two heteroatoms are associated with the vertices r and t. Thus the resulting graph G^{rt} possesses two self-loops on the vertices r and t; their weights are h_r and h_t, respectively [7, 8]. Then the characteristic polynomial of G^{rt} conforms to the identity

$$\phi(G^{rt}) = \phi(G) - h_r\,\phi(G-r) - h_t\,\phi(G-t) + h_r\,h_t\,\phi(G-r-t), \tag{1}$$

where $G-r$ denotes the subgraph obtained by deleting from G the vertex r; the meaning of $G-t$ and $G-r-t$ is analogous.

We introduce an auxiliary graph invariant (G) related to the characteristic polynomial via

$$(G) = i^{-n}\,\phi(G, i\,x), \tag{2}$$

where $i = \sqrt{-1}$. If G is a bipartite graph then (G) has the following two important properties:

(i) Considered as a function of the variable x, (G) is a monic polynomial of degree n all the coefficients of which are non-negative integers.

(ii) If n is even then (G) is an even function of x. If n is odd then (G) is an odd function of x.

By use of definition (2), (1) is easily transformed into

$$(G^{rt}) = (G) + i\,h_r(G-r) + i\,h_t(G-t) - h_r\,h_t(G-r-t). \tag{3}$$

Reprint requests to Prof. Dr. Ivan Gutman, Faculty of Science, P.O. Box 60, YU-34000 Kragujevac, Jugoslavia

0932-0784 / 90 / 0900-1085 $ 01.30/0. – Please order a reprint rather than making your own copy

Denote by $\alpha(G, x) = \alpha(G)$ the matching polynomial of G [9] and introduce another graph invariant $[G]$:

$$[G] = i^{-n}\, \alpha(G, i\,x). \tag{4}$$

The basic properties of $[G]$ are completely analogous to that of (G):

[i] Considered as a function of the variable x, $[G]$ is a monic polynomial of degree n, all the coefficients of which are non-negative integers.

[ii] If n is even then $[G]$ is an even function of x. If n is odd then $[G]$ is an odd function of x.

Furthermore, in parallel to (1) and (3) we have

$$\begin{aligned}\alpha(G^{rt}) = \alpha(G) - h_r\, \alpha(G-r) - h_t\, \alpha(G-t)\\ + h_r\, h_t\, \alpha(G-r-t),\end{aligned} \tag{5}$$

$$\begin{aligned}[][G^{rt}] = [G] + i\, h_r [G-r] + i\, h_t [G-t]\\ - h_r\, h_t\, [G-r-t].\end{aligned} \tag{6}$$

Recall that [i] and [ii] hold for arbitrary graphs G whereas (i) and (ii) apply only to bipartite graphs.

Graph Propagators

As already mentioned, the concept of graph propagators seems to have been invented by Merrifield and Simmons and first publicized in their outstanding book [6]. They defined the propagator for the number of independent-vertex sets of a graph. We extend their idea and slightly modify it so as to apply to an arbitrary graph invariant.

Let $I(G)$ be a graph invariant associated with the graph G. Let u and v be two distinct vertices of G. Then the quantity

$$\begin{aligned}\gamma_{uv}(G) = \gamma_{uv}(G; I) = I(G-u)\, I(G-v)\\ - I(G)\, I(G-u-v)\end{aligned}$$

will be called the propagator of the graph G (corresponding to I) or more precisely the (u, v)-element of the propagator matrix.

In this work we are interested in the propagators corresponding to the characteristic and matching polynomials as well as to the polynomials (G) and $[G]$. The reason for this are the two identities

$$\phi(G-u)\, \phi(G-v) - \phi(G)\, \phi(G-u-v) = \Big\{\sum_W \phi(G-W)\Big\}^2 \tag{7}$$

and

$$\alpha(G-u)\, \alpha(G-v) - \alpha(G)\, \alpha(G-u-v) = \sum_W \{\alpha(G-W)\}^2. \tag{8}$$

The right-hand side summations in (7) and (8) go over all paths of the graph G which connect the vertices u and v (for an illustrative example see [3]). Formula (7) is in an implicit form contained in the paper [10] of Coulson and Longuet-Higgins (for details see [3]). Formula (8) was discovered by Heilmann and Lieb [11].

By means of (2) and (4) the above relations are transformed into

$$(G-u)(G-v) - (G)(G-u-v) = (-1)^{d(u,v)} \Big\{\sum_W (G-W)\Big\}^2 \tag{9}$$

and

$$[G-u]\,[G-v] - [G]\,[G-u-v] = (-1)^{d(u,v)} \sum_W [G-W)^2, \tag{10}$$

where $d(u, v)$ is the distance between the vertices u and v. We used the fact that in bipartite graphs the number of vertices in all paths connecting the vertices u and v has the same parity as $d(u, v) - 1$.

In what follows the propagators $(G-u)(G-v) - (G)(G-u-v)$ and $[G-u]\,[G-v] - [G]\,[G-u-v]$ will be denoted by (γ_{uv}) and $[\gamma_{uv}]$, respectively. From (9) and (10) we immediately see that the signs of (γ_{uv}) and $[\gamma_{uv}]$ depend exclusively on the distance between the vertices u and v, namely

$$\operatorname{sign}(\gamma_{uv}) = \operatorname{sign}[\gamma_{uv}] = (-1)^{d(u,v)}. \tag{11}$$

Collective Effect of Two Heteroatoms on Total π-Electron Energy

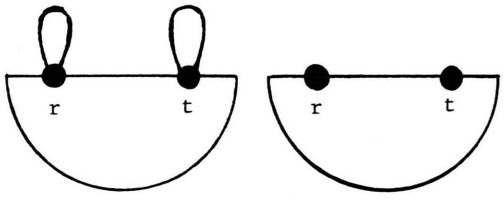
In order to measure the collective effect of two heteroatoms on the total π-electron energy of a conjugated molecule, we have to compare the energies of the systems $G^{rt} \cup G$ and $G^r \cup G^t$.

Evidently, $E(G^{rt} \cup G) = E(G^{rt}) + E(G)$ whereas $E(G^r \cup G^t) = E(G^r) + E(G^t)$. If there were no interaction between the heteroatoms r and t, then these two energies would be equal. Their difference is given by [12, 13]

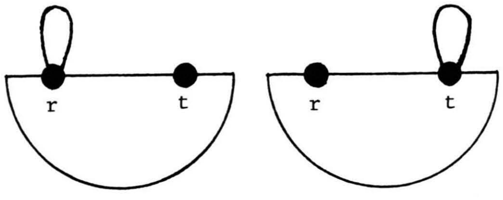
$$\Delta E = \left\langle \log \frac{\phi(G^{rt}, i\,x)\, \phi(G, i\,x)}{\phi(G^r, i\,x)\, \phi(G^t, i\,x)} \right\rangle = \left\langle \log \frac{(G^{rt})\,(G)}{(G^r)\,(G^t)} \right\rangle, \tag{12}$$

where $\langle F \rangle$ is an abbreviation for $(1/\pi) \int_{-\infty}^{+\infty} F(x)\, dx$.

We note in passing that formula (12) is obtained by using the contour integral method invented by Coulson in 1940 [14]; for details see [15].



G^{rt} U G



G^{r} U G^{t}

Using the relations [1, 2]

$$\phi(G^{\lambda}) = \phi(G) - h_{\lambda}\, \phi(G-\lambda),$$
$$(G^{\lambda}) = (G) + i\, h_{\lambda}\, (G-\lambda), \quad \lambda = r, t$$

and the fact that ΔE is a real-valued quantity we obtain

$$\Delta E = \tfrac{1}{2}\langle \log\{[1 + h_r\, h_t (\gamma_{rt})\, \{(G)^2 - h_r\, h_t (G-r) \cdot (G-t)\} X^{-1}]^2 + \{h_r (G-r) + h_t (G-t)\}^2\, X^{-2}\}\rangle. \tag{13}$$

where

$$X = \{(G)^2 - h_r\, h_t (G-r)\,(G-t)\}^2 + \{h_r (G-r) + h_t (G-t)\}^2 .$$

For large values of x the function X behaves as $(G)^4$, i.e. as x^{4n}. Therefore the integrand in (13) may be simplified by using the approximation $\log(1+y) \approx y$. This results in

$$\Delta E = \Delta E_1 + \Delta E_2 ,$$

where

$$\Delta E_1 = h_r h_t \langle (\gamma_{rt})\, \{(G)^2 - h_r\, h_t (G-r)\,(G-t)\} X^{-1}\rangle,$$
$$\Delta E_2 = \tfrac{1}{2}\langle \{h_r\, h_t (\gamma_{rt})\}^2\, \{(G)^2 - h_r\, h_t (G-r)\,(G-t)\}^2 X^{-2} + \{h_r (G-r) + h_t (G-t)\}^2\, X^{-2}\}\rangle.$$

Note that ΔE_2 is necessarily positive because its integrand is a positive-valued function. The integrand in ΔE_1 behaves asymptotically as $h_r\, h_t (\gamma_{rt})(G)^{-2}$ whereas the integrand in ΔE_2 is roughly proportional to $\{h_r\, h_t (\gamma_{rt})\}^2 (G)^{-4}$. Therefore ΔE_2 is much smaller than $|\Delta E_1|$. Besides, because of (11),

$$\operatorname{sign} \Delta E_1 = (-1)^{d(r,t)} \operatorname{sign}(h_r\, h_t).$$

We are now prepared to formulate our first general rule.

Rule 1. The dominant term in the collective effect of two heteroatoms on the total π-electron energy (ΔE_1) is positive if

(a) h_r and h_t have equal signs and the distance between the heteroatoms is even, or

(b) h_r and h_t have different signs and the distance between the heteroatoms is odd.

In all other cases ΔE_1 is negative.

We wish to remind that positive contributions to the total π-electron energy increase the thermodynamic stability of the respective heteroconjugated molecule; negative-valued contributions act in the opposite direction.

Collective Effect of Two Heteroatoms on Resonance Energy

In line with the arguments given in the previous section we consider here the difference ΔRE between the resonance energies of G^{rt} U G and G^{r} U G^{t}. We employ the "topological" resonance energy (TRE) model [16–18], according to which

$$\Delta RE = \Delta E - \Delta E^{*},$$

where ΔE is given by (12) whereas ΔE^{*} satisfies an analogous relation [15, 16]:

$$\Delta E^{*} = \left\langle \log \frac{\alpha(G^{rt}, i x)\, \alpha(G, i x)}{\alpha(G^{r}, i x)\, \alpha(G^{t}, i x)} \right\rangle = \left\langle \log \frac{[G^{rt}]\,[G]}{[G^{r}]\,[G^{t}]} \right\rangle.$$

Consequently ΔE^{*} is the collective effect of the two heteroatoms on the energy of the reference structure.

Bearing in mind (5), (6) and

$$\alpha(G^{\lambda}) = \alpha(G) - h_{\lambda}\, \alpha(G-\lambda),$$
$$[G^{\lambda}] = [G] + i\, h_{\lambda}\, [G-\lambda], \quad \lambda = r, t,$$

we conclude that ΔE^{*} must have a form analogous to (13), namely

$$\Delta E^{*} = \tfrac{1}{2}\langle \log\{[1 + h_r\, h_t [\gamma_{rt}]\, \{[G]^2 - h_r\, h_t [G-r] \cdot [G-t]\}\, Y^{-1}]^2 + \{h_r [G-r] + h_t [G-t]\}^2\, Y^{-2}\}\rangle,$$

where

$$Y = \{[G]^2 - h_r\, h_t [G-r]\,[G-t]\}^2 + \{h_r [G-r] + h_t [G-t]\}^2 .$$

As a good approximation

$$\Delta E^* = \Delta E_1^* + \Delta E_2^*,$$

where

$$\Delta E_1^* = h_r h_t \langle [\gamma_{rt}] \{[G]^2 - h_r h_t [G-r][G-t]\} Y^{-1} \rangle,$$

$$\Delta E_2^* = \tfrac{1}{2} \langle \{h_r h_t [\gamma_{rt}]\}^2 \{[G]^2 - h_r h_t [G-r][G-t]\}^2 Y^{-2} + \{h_r [G-r] + h_t [G-t]\}^2 Y^{-2}\} \rangle.$$

The previous conclusions about the sign and magnitude of ΔE_1 and ΔE_2 can be simply extended to ΔE_1^* and ΔE_2^*, respectively. In particular, $\Delta E_2^* \ll |\Delta E_1^*|$ and

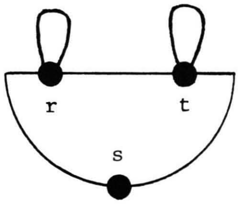
$$\operatorname{sign} \Delta E_1^* = (-1)^{d(r,t)} \operatorname{sign}(h_r h_t).$$

Rule 2. The dominant term in the collective effect of two heteroatoms on the energy of the reference structure in the *TRE* model (ΔE_1^*) is positive in precisely the same cases as ΔE_1 (see Rule 1).

Because *TRE* is the difference between the total π-electron energy of the molecule considered and the energy of the respective reference structure [14, 16], the effects described in Rules 1 and 2 will cancel each other (although not completely). As a consequence the collective effect of two heteroatoms on the "topological" resonance energy (ΔRE) is much smaller than the effects on both the total energy (ΔE) and the reference energy (ΔE^*) and is probably of no chemical significance. In other words, the expression $TRE(G^r) + TRE(G^t) - TRE(G)$ is a reasonably good approximation for the resonance energy of a heteroconjugated molecule with two heteroatoms.

Collective Effect of Two Heteroatoms on π-Electron Charge Distribution

In this section we examine the π-electron charge Q_s on the atom s of the heteroconjugated system the molecular graph of which is G^{rt} (i.e. in which the heteroatoms occupy the positions r and t).



G^{rt}

Employing the Coulson-Longuet-Higgins integral formula [10]

$$Q_s = \langle \phi(G^{rt} - s, ix) / \phi(G^{rt}, ix) \rangle$$

and using (1)–(3) one arrives at

$$Q_s = Q_{s1} + Q_{s2} + Q_{s3} + Q_{s4}, \tag{14}$$

where

$$Q_{s1} = -h_r \langle (\gamma_{rs})/Z \rangle,$$

$$Q_{s2} = -h_r h_t^2 \langle (\gamma_{rs} - t)/Z \rangle,$$

$$Q_{s3} = -h_t \langle (\gamma_{ts})/Z \rangle,$$

$$Q_{s4} = -h_r^2 h_t \langle (\gamma_{ts} - r)/Z \rangle,$$

and

$$Z = \{(G) - h_r h_t (G-r-t)\}^2 + \{h_r (G-r) + h_t (G-t)\}^2.$$

In the above formulae $(\gamma_{rs} - t)$ and $(\gamma_{ts} - r)$ are shorthand notations for the propagators (γ_{rs}) and (γ_{ts}) of the graphs $G-t$ and $G-r$, respectively:

$$(\gamma_{rs} - t) = (G-r-t)(G-s-t) - (G-t)(G-r-s-t),$$

$$(\gamma_{ts} - r) = (G-t-r)(G-s-r) - (G-r)(G-t-s-r).$$

We first point out the fact that in the limit when h_r and h_t tend to zero, the integral $\langle (\gamma_{rs})/Z \rangle$ becomes equal to the atom-atom polarizability π_{rs},

$$\pi_{rs} = \langle (\gamma_{rs})/(G)^2 \rangle.$$

This latter formula (without using the propagator concept) was already reported as (2) of [3].

Whence we see that the first-order perturbation formula

$$Q_s = -h_r \pi_{rs} - h_t \pi_{ts}$$

is obtained by neglecting h_r and h_t in Z and by neglecting Q_{s2} and Q_{s4} in (14).

From (14) is evident how the charge on the atom s is induced by the heteroatoms in positions r and t. The terms Q_{s1} and Q_{s3} describe the direct influence of the two heteroatoms; they are roughly proportional to the respective atom-atom polarizabilities. On the other hand Q_{s2} and Q_{s4} correspond to the collective effects of the two heteroatoms. It is remarkable that the signs of the two collective-effect terms fully coincide with the signs of the two individual-effect terms. This means that in formula (14) the collective effect of the two heteroatoms is separated in two parts: one (Q_{s2}) acting in the same direction as the first heteroatom (r), the other (Q_{s4}) enhancing the effect of the second heteroatom (t).

A more detailed analysis of (14) reveals the following general regularities:

Rule 3. (a) If h_r and h_t have equal signs and the distance between the heteroatoms is even, then

$$\operatorname{sign} Q_s = -(-1)^{d(r,s)} \operatorname{sign} h_r = -(-1)^{d(t,s)} \operatorname{sign} h_t .$$

The same sign rule holds also if h_r and h_t have different signs and the distance between the heteroatoms is odd.

(b) If h_r and h_t have equal signs and the distance between the heteroatoms is odd, or if h_r and h_t have different signs and the distance between the heteroatoms is even, then the heteroatoms induce opposite π-electron charges on the atom s and the sign of the resulting charge depends on the numerical values of the parameters h_r and h_t, on the structure of the molecular graph G and on the position of the vertex s in G. In other words, the sign of the π-electron charge cannot be predicted by simple topological rules.

Concluding Remarks

The study of topological properties of alternant conjugated molecules with two heteroatoms (as well as with one heteroatom [3]) revealed the important role which graph propagators play (or should play) in chemical graph theory. By means of graph propagators we were able to simplify various perplexed topological expressions and to extract from them certain general rules.

Graph propagators deserve more attention from theoretical chemists and one might hope that their study will yield many more novel results.

Acknowledgement

The financial support of this research by the Fulbright Program is gratefully acknowledged.

[1] Part I: I. Gutman and S. Bosanac, Chem. Phys. Letters **43,** 371 (1976).
[2] Part II: I Gutman, Theor. Chim. Acta **50,** 287 (1979).
[3] Part III: I. Gutman, Z. Naturforsch. **36a,** 1112 (1981).
[4] Part IV: I. Gutman, Bull. Soc. Chim. Beograd **49,** 157 (1984).
[5] Part V: I. Gutman, Z. Naturforsch. **39a,** 152 (1984).
[6] R. E. Merrifield and H. E. Simmons, Topological Methods in Chemistry, Wiley, New York 1989.
[7] C. A. Coulson, B. O'Leary and R. B. Mallion, Hückel Theory for Organic Chemists, Academic Press, London 1978.
[8] R. B Mallion, N. Trinajstić and A. J. Schwenk, Z. Naturforsch. **29a,** 1481 (1974).
[9] C. D. Godsil and I. Gutman, J. Graph. Theory **5,** 137 (1981).
[10] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. London **A191,** 39 (1947).
[11] O. J. Heilmann and E. H. Lieb, Commun. Math. Phys. **25,** 190 (1972).
[12] C. A. Coulson, J. Chem. Soc. **1954,** 3111.
[13] R. A. Marcus, J. Chem. Phys. **43,** 2643 (1965).
[14] C. A. Coulson, Proc. Cambridge Phil. Soc. **36,** 201 (1940).
[15] B. O'Leary and R. B. Mallion, J. Math. Chem. **3,** 323 (1989).
[16] J. Aihara, J. Amer. Chem. Soc. **98,** 2750 (1976).
[17] I. Gutman and N. Trinajstić, Acta Chim. Hung. **91,** 203 (1976).
[18] I. Gutman, M. Milun, and N. Trinajstić, J. Amer. Chem. Soc. **99,** 1692 (1977).