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New Applications of the Dewar Index

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It is demonstrated that the Dewar index D plays an important role also in non-perturbative MO theory. Approximate topological formulas are derived for the stability of a heteroconjugated molecule relative to its parent hydrocarbon (eq 12), the self-polarizability of an atom (eq 13) and the atom localization energy (eq 16). All three quantities are shown to depend on D.

These relations hold for alternant systems only. Their numerical reliability is also studied.

INTRODUCTION

It is usually believed that the Dewar index (D) may be used for the prediction of the stability of conjugated compounds, only within the framework of perturbation molecular orbital (PMO) method[1]. The aim of the present work is to demonstrate that this topological index might have a much deeper theoretical meaning and practical importance. In particular, we offer topological formulas which show that certain, seemingly unrelated quantities in non-perturbative MO theory depend on D.

Let a conjugated hydrocarbon H be obtained by joining a new carbon atom p to the atoms a, b, ... of a conjugated radical R. In the PMO approximation[1], the total π-electron energy (in β units) of H is

$$E(\mathrm{H}) \doteq E(\mathrm{R}) + 2(\mathrm{C_a} + \mathrm{C_b} + \ldots)$$

where $E(\mathrm{R})$ is the total π-electron energy of the radical R and $\mathrm{C_a}$, $\mathrm{C_b}$, ... are the coefficients of the (normalized) non-bonding molecular orbital (NBMO) of R, corresponding to the atoms a, b, ... Since the localization energy of the site p of the molecule H is $L_p = E(\mathrm{H}) - E(\mathrm{R})$, we have

$$L_p \doteq 2(\mathrm{C_a} + \mathrm{C_b} + \ldots)$$

The quantity $D = D_p = 2(\mathrm{C_a} + \mathrm{C_b} + \ldots)$ is called the *Dewar index*. The subscript p indicates that it corresponds to a particular site p of the molecule. When not necessary, the subscript will be omitted.

NOTATION AND DEFINITIONS

It is convenient to use graph-theoretical notation and terminology.[2] Hence, the hydrocarbon H (with N carbon atoms) is represented by a graph G (with N vertices). The representation of R is then the graph G-p, obtained by deletion of the vertex p from G. The adjacency matrix $\mathbf{A}(G)$ of G is defined by

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$$[\mathbf{A}(G)]_{rs} = \begin{cases} 1 & \text{if the vertices } r \text{ and } s \text{ are adjacent in } G \\ 0 & \text{otherwise} \end{cases}$$

The characteristic polynomial of G is $P(G, x) = \det(x\mathbf{I} - \mathbf{A})$. If G represents an alternant system (which will be assumed throughout this paper), $P(G, x)$ may be written in the form

$$P(G, x) = x^N - a_2 x^{N-2} + a_4 x^{N-4} - \ldots + (-1)^{N/2} a_N \tag{1}$$

Similarly,

$$P(G - p, x) = x^{N-1} - b_2 x^{N-3} + b_4 x^{N-5} - \ldots + (-1)^{N/2-1} b_{N-2}\, x \tag{2}$$

In this notation the coefficients a_{2j} and b_{2j} are necessarily non-negative. Besides, if R has a unique NBMO, $b_{N-2} \neq 0$.

If the p-th carbon atom in the hydrocarbon H is replaced by a heteroatom, a heteroconjugated molecule is obtained. Its graph representation[3] is a rooted graph G_h with a self-loop of weight h on the vertex p. In matrix notation,

$$[\mathbf{A}(G_h)]_{rs} = \begin{cases} h & \text{for } r=s=p \\ [\mathbf{A}(G)]_{rs} & \text{otherwise} \end{cases}$$

Of course, for $h = 0$, G_h becomes equal to G. A well known[3] recursion relation for the characteristic polynomial of G_h is of the form

$$P(G_h, x) = P(G, x) - h\, P(G - p, x) \tag{3}$$

The relations between the Dewar index and molecular topology were analysed in more detail in a recent paper.[4] For the purposes of the present discussion note that

$$D_p = 2\, \frac{\mathrm{ASC}\,(G)}{\mathrm{asc}\,(G - p)} \tag{4}$$

where ASC and asc, the algebraic structure count and its generalization, are defined in refs 4 and 5. Further[5],

$$[\mathrm{ASC}\,(G)]^2 = a_N \quad \text{and} \quad [\mathrm{asc}\,(G - p)]^2 = b_{N-2}$$

where a_N and b_{N-2} are the last coefficients in eqs 1 and 2. This gives as a final result

$$D = 2 \left[\frac{a_N}{b_{N-2}} \right]^{1/2} \tag{5}$$

THE RELATION BETWEEN *D* AND THE STABILITY OF A HETEROCONJUGATED MOLECULE RELATIVE TO ITS PARENT HYDROCARBON

Let G_h and G be the graphs of a heteroconjugated molecule (with one heteroatom) and its parent hydrocarbon, respectively. The difference $E(G_h) - E(G)$ is thus the measure of the stability of the heteroconjugated molecule relative to its parent hydrocarbon.

If G_a and G_b are graphs with an equal number of vertices, the following formula holds[6]:

$$E(G_a) - E(G_b) = \langle \log \left| \frac{P(G_a, ix)}{P(G_b, ix)} \right| \rangle \tag{6}$$

where $i = \sqrt{-1}$. Here and later on we use the abbreviate notation

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

From eqs 1, 2 and 3, after suitable transformations, we obtain

$$E(G_h) - E(G) = h + 1/2 \langle \log (1 + h^2 V^2) \rangle$$

where

$$V = V(x) = \frac{x^{N-1} + b_2 x^{N-3} + b_4 x^{N-5} + \ldots + b_{N-2} x}{x^N + a_2 x^{N-2} + a_4 x^{N-4} + \ldots + a_N} \tag{7}$$

It can be proved[7] that the function $V(x)$ has following properties

$$V(x) \sim \begin{cases} \dfrac{b_{N-2}}{a_N} x = \dfrac{4x}{D^2} & \text{for small } |x| \\ 1/x & \text{for large } |x| \end{cases} \tag{8}$$

since according to eq 5, it is $b_{N-2}/a_N = 4/D^2$. Therefore,

$$\log (1 + h^2 V^2) \sim \begin{cases} 16\, h^2 x^2/D^4 & \text{for small } |x| \\ h^2/x^2 & \text{for large } |x| \end{cases} \tag{9}$$

Because of (9), the function $\log (1 + h^2 V^2)$ has a maximum for some x in the interval $(0, \infty)$, say for $x = x_m$. Neither x_m nor $\log (1 + h^2 V^2 (x_m))$ can be expressed in a simple manner. In the first approximation, however, the position of the maximum can be guessed by equating $16\, h^2 x^2/D^4$ with h^2/x^2. Hence,

$$x_m \doteq D/2 \tag{10}$$

Let us consider a simple algebraic function

$$V_0 = V_0(x) = \frac{4x}{D^2 + 4x^2} \tag{11}$$

It can be demonstrated by elementary methods that behaviour of $V_0(x)$ for small and large $|x|$ is the same as that of $V(x)$. Besides, the function $\log (1 + h^2 V_0^2)$ has a unique maximum in the interval $(0, \infty)$. The position of this maximum is $x_m = D/2$, which should be compared with relation 10.

The integral $\langle \log (1 + h^2 V^2) \rangle$ can therefore, be approximated[8] by $\langle \log (1 + h^2 V_0^2) \rangle$. The reliability of this approximation will mainly depend on the extent to which relation 10 is correct. A numerical analysis of such treatment will be given in one of the following sections.

Application of eq A1 from the *Appendix* gives

$$\langle \log (1 + h^2 V_0^2) \rangle = 2 \sqrt{D^2 + h^2} - 2D$$

and finally,

$$E(G_h) - E(G) \doteq h + \sqrt{D^2 + h^2} - D \tag{12}$$

As a consequence of formula 12, among positional isomers with one heteroatom, the most (least) stable one should be that with the heteroatom in the position with minimal (maximal) Dewar index.

THE RELATION BETWEEN *D* AND THE SELF-POLARIZABILITY OF THE ATOM

Coulson and Longuet-Higgins proved[9] that the self-polarizability of the atom *p* in a conjugated molecule is given by

$$\pi_{pp} = - < \left[\frac{P(G-p, ix)}{P(G, ix)} \right]^2 >$$

Of course, the original result of ref 9 is here translated into the language of graph theory.[2,10]

It is now easily sêen that this expression reduces to

$$\pi_{pp} = \langle V^2 \rangle$$

where the function *V* is defined by eq 7. Hence, $<V_0^2>$ will be a good approximation for π_{pp} with V_0 being given by eq 11. Straightforward integration gives

$$\pi_{pp} \doteq 1/D_p \tag{13}$$

The reliability of this rather simple approximate expression will be discussed later. Note that the same formula for π_{pp} can be obtained from eq 12, knowing that[9]

$$\pi_{pp} = \left[\frac{d^2}{dh^2} \mathrm{E}(G_h) \right]_{h=0}$$

THE RELATION BETWEEN *D* AND THE ATOM LOCALIZATION ENERGY

In PMO theory D_p is (by definition) equal to the localization energy L_p of the *p*-th carbon atom of the hydrocarbon H. Previous non-perturbative MO considerations[4] resulted in a semiempirical formula for L_p, with a logarithmic dependence on D_p. However, this formula is to some extent arbitrary because it is obtained under the *assumption* that the total π-electron energy is linearly proportional to log (ASC).[11] In the present section we offer a non-empirical approach to the same problem.

Let *G* be the molecular graph and *G*-(*p*) the graph obtained by deletion of all edges incident to the vertex *p*. If $d = d_p$ is the degree of the vertex *p*, there are exactly *d* edges incident to *p*. Note that $a_2 - b_2 = d$, where a_2 and b_2 are coefficients of the characteristic polynomials (1) and (2). *G*-(*p*) is the union of the graph *G*-*p* and the isolated vertex *p*. Consequently, $P(G\text{-}(p), x) = x P(G\text{-}p, x)$.

The localization energy L_p of the site *p* is just equal to $E(G) - E(G\text{-}(p))$. Since *G* and *G*-(*p*) contain an equal number of vertices, the application of eq 6 gives

$$L_p = \langle \log W \rangle \tag{14}$$

with

$$W = W(x) = \left| \frac{P(G, ix)}{P(G-(p), ix)} \right|$$

Analysis shows that

$$W(x) \sim \begin{cases} D^2/(4x^2) & \text{for small } |x| \\ 1 + \dfrac{d}{x^2} & \text{for large } |x| \end{cases} \tag{15}$$

We may, therefore approximate[8] the integral (14) by $\langle \log W_0 \rangle$, where

$$W_0 = W_0(x) = \frac{x^4 + (d+1)\,x^2 + D^2/4}{x^4 + x^2}$$

Calculation based on eq A1 of *Appendix* results in the following topological formula

$$L_p \doteq 2\sqrt{D_p + d_p + 1} - 2 \tag{16}$$

Note that almost in all cases of chemical interest it is $d_p = 2$.

NUMERICAL WORK

The aim of the present work was to investigate the topological background of certain MO quantities, and to demonstrate their mutual relations rather than generate formulas for quick hand calculation. Nevertheless, it is instructive to test formulas (12), (13) and (16) numerically, in order to see their reliability.

An arbitrarily chosen set of 12 alternant conjugated hydrocarbons (6 benzenoid, 3 acyclic and 3 ciclobutadiene containing systems) was studied. It has been found that eq 13 overestimates π_{pp} in all cases with an average violation of about 25%. Moreover, there exists no satisfactory correlation between exact π_{pp} values and those calculated by eq 13, which indicates that $V(x)$ and $V_0(x)$ are maximal for considerably different values of x. Hence, eq 13 is to be used only for qualitative purposes.

Eq 16 also overestimates the corresponding L_p values. However, after an empirical correction

$$L_p \doteq 2\sqrt{D_p + d_p + 1} - 2.075 \tag{17}$$

localization energies are reproduced with an average error of only 1.5% (that is up to a few hundredth of β).

Eq 12 was tested for nitrogen-containing heterocycles[12], assuming the value of $h = 0.4$.[13] It has been found that the formula reproduces the $E(G_h) - E(G)$ differences up to a few thousandths of β (average error of 1.9%). This may be understood as a partial confirmation of eq 10, namely that both $\log(1 + h^2 V^2)$ and $\log(1 + h^2 V_0^2)$ have their maxima at nearly the same point. Hence, eqs 12 and 17 are applicable for *paper and pencil* numerical evaluation of $E(G_h) - E(G)$ and L_p.

DISCUSSION

Three novel topological formulas (12), (13) and (16) have been derived, which indicate that D is closely related with various MO indices. These quantities, of course, correspond to a given site of the molecule considered. Thus we may conclude that the chemical behaviour[14] of a conjugated centre is to a high extent determined by its D value.

In non-alternant systems, another important MO index is the π-electron charge density Q_p. (As well known[14], $Q_p = 1$ in all alternants.) One may speculate about the possibility that also Q_p is a simple function of the Dewar index. A support for such an expectation is the relation[9]

$$Q_p = \left[\frac{d}{dh} E(G_h) \right]_{h=0}$$

However, our experience (both numerical and graph-theoretical) indicates that this will not be the case.

In fact, the original definition[1] of the Dewar index requires the existence of a (unique) NBMO in the radical R. If R is not alternant, it needs not possess any NBMO.[15] Moreover, in the general case of a non-alternant topology, neither eq 4 nor eq 5 are valid.[16] Similarly, the conditions (8), (9) and (15), which are crucial for the derivation of our topological formulas, are not true for non-alternants. Thus the problem of the extension of the present considerations to non-alternant systems remains unsolved.

The existence of formulas (12), (13) and (16) may be understood as partial justification of the success of the perturbation molecular orbital theory.

APPENDIX

We prove that

$$\left\langle \log \frac{x^4 + S_1 x^2 + S_2}{x^4 + S_3 x^2 + S_4} \right\rangle = 2 \sqrt{S_1 + 2 \sqrt{S_2}} - 2 \sqrt{S_3 + 2 \sqrt{S_4}} \qquad \text{(A1)}$$

The integrand in eq A1 can also be written in the form

$$U(x) = \log \frac{(x^2 + T_1^2)(x^2 + T_2^2)}{(x^2 + T_3^2)(x^2 + T_4^2)}$$

where, of course,

$$T_1^2 + T_2^2 = S_1 \qquad (T_1 T_2)^2 = S_2$$

$$T_3^2 + T_4^2 = S_1 \qquad (T_3 T_4)^2 = S_4$$

Now,

$$\int \log (x^2 + T^2) \, dx = x \log (x^2 + T^2) - 2x + 2T \operatorname{arctg} (x/T)$$

and consequently,

$$\int U(x) \, dx = x \, U(x) + 2T_1 \operatorname{arctg} (x/T_1) + 2T_2 \operatorname{arctg} (x/T_2) - \\ - 2T_3 \operatorname{arctg} (x/T_3) - 2T_4 \operatorname{arctg} (x/T_4)$$

Since $x \, U(x) \to 0$ for $|x| \to \infty$, we get

$$\int_{-\infty}^{+\infty} U(x) \, dx = 2\pi (T_1 + T_2 - T_3 - T_4) = 2\pi \left(\sqrt{T_1^2 + T_2^2 + 2 T_1 T_2} - \\ - \sqrt{T_3^2 + T_4^2 + 2 T_3 T_4} \right) = 2\pi \left(\sqrt{S_1 + 2 \sqrt{S_2}} - \sqrt{S_3 + 2 \sqrt{S_4}} \right)$$

However, this is just eq A1 in another notation.

REFERENCES

1. M. J. S. Dewar, *J. Amer. Chem. Soc.* **74** (1952) 3345, 3357; M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGrow-Hill, New York 1969, §§ 6.10—6.13.
2. For a review on the application of graphs in the theory of conjugated compounds see: I. Gutman and N. Trinajstić, *Topics Curr. Chem.* **42** (1973) 49; *Croat. Chem. Acta* **47** (1975) 507.
3. R. B. Mallion, A. J. Schwenk, and N. Trinajstić, *Croat. Chem. Acta* **46** (1974) 171; R. B. Mallion, N. Trinajstić, and A. J. Schwenk, *Z. Naturforsch.* **29 a** (1974) 1481.
4. C. F. Wilcox, Jr., I. Gutman, and N. Trinajstić, *Tetrahedron* **31** (1975) 147.
5. I. Gutman, N. Trinajstić, and C. F. Wilcox, Jr., *ibid.* **31** (1975) 143.
6. C. A. Coulson, *J. Chem. Soc.* (1954) 3111; see also: R. A. Marcus, *J. Chem. Phys.* **43** (1965) 2643.
7. I. Gutman and S. Bosanac, *Chem. Phys. Letters* **43** (1976) 371.
8. This technique for approximation of integrals $<F(x)>$ is elaborated in: I. Gutman, *J. Chem. Phys.* **66** (1977) 1652.
9. C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London) **A 191** (1947) 39.
10. I. Gutman and N. Trinajstić, *J. Chem. Phys.* **65** (1976) 3796.
11. See eq 11 of ref 4. Note also that both eqs 11 and 14 in ref 4 contain the parameters A, B and C, which are to be determined empirically.
12. G. Derflinger, W. Jakubetz, H. Lischka, and O. E. Polansky, *HMO-Tabellen. Hückel-Molekülorbitale von Stickstoff-Heterocyclen,* Institut für Strahlenchemie, Mülheim ad. d. Ruhr 1974.
13. The parametrisation scheme $\alpha_N = \alpha_C + 0.4\,\beta_{CC}$ and $\beta_{CN} = \beta_{CC}$ is found to be optimal for nitrogen-containing heterocycles: B. Pullman and A. Pullman, *Quantum Biochemistry,* Interscience, New York 1963.
14. The relations which exist between the reactivity of a site p of a conjugated system and the corresponding π_{pp}, L_p and Q_p values are well known. See for example: K. Higasi, H. Baba, and A. Rembaum, *Quantum Organic Chemistry,* Interscience, New York 1965, Chapter 11; J. N. Murrel, S. F. A. Kettle, and J. M. Tedder, *Valence Theory,* Wiley, London 1965, Chapter 17.
15. W. C. Herndon, *Tetrahedron* **28** (1972) 3675.
16. C. F. Wilcox, Jr., *J. Amer. Chem. Soc.* **91** (1969) 2732; I. Gutman and N. Trinajstić, *Croat. Chem. Acta* **47** (1975) 35.

SAŽETAK

Nove primjene Dewarova broja

I. Gutman

Pokazano je da Dewarov broj *D* igra znatnu ulogu i u ne-perturbacijskoj teoriji molekulskih orbitala. Dobivene su približne topološke formule za promjenu stabilnosti spoja zbog uvođenja heteroatoma u konjugirani ugljikovodik (jedn. 12), za samopolarizabilnost atoma (jedn. 13) te za atomsku lokalizacijsku energiju (jedn. 16). Sve ove tri veličine ovise o *D*.

Dobivene relacije važe samo za alternantne sustave.

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