Theoret. Chim. Acta (Berl.) 47, 217–222 (1978)

THEORETICA CHIMICA ACTA

Bounds for Reactivity Indices

Ivan Gutman*

Institut für Quantenchemie, Freie Universität Berlin,
Holbeinstr. 48, D-1000 Berlin, Federal Republic of Germany

Lower and upper bounds are derived for bond number, localization energy and atom self-polarizability of alternant hydrocarbons. It is proved that in acyclic polyenes the maximal bond number is 1, $\sqrt{2}$ and $\sqrt{3}$, respectively for primary, secondary and tertiary carbon atoms.

Key words: Graph theory – Free valence – Localization energy – Polarizability

1. Introduction

In the molecular orbital theory of organic molecules [1], several reactivity indices have been defined which are expected to parallel the chemical behaviour of conjugated compounds. Bond number N_r, free valence F_r, localization energy L_r and atom self-polarizability π_{rr} are the important reactivity indices for a particular site of an alternant hydrocarbon. They are defined as

$$N_r = \sum_s p_{rs}$$

$$F_r = N_{\max} - N_r$$

$$L_r = E - E_r$$

$$\pi_{rr} = \frac{1}{2} \frac{\partial^2 E}{\partial \alpha_r^2}$$

In the above formulas, p_{rs} is the bond order between the atoms r and s and the summation goes over all atoms s adjacent to r; $N_{\max}$ is the maximal possible bond

---

* Alexander von Humboldt Fellow. Permanent address: Department of Chemistry, Faculty of Sciences, University of Kragujevac, 34000 Kragujevac, R. Domanovića 12, Yugoslavia.

0040-5744/78/0047/0217/$01.20

number; E and E_r are the total π electron energy of the molecule and of its corresponding σ complex; α_r is the Coulomb integral at site r [1]. In spite of the apparently dissimilar form of these equations, they give strongly correlated numerical results, especially when applied to alternant systems [2, 3]. These indices have also a similar functional dependence on molecular topology, which can be immediately seen by comparison of the integral expressions (2–4).

In the present paper we shall use standard graph-theoretical terminology [4]. Thus a conjugated hydrocarbon is represented by its molecular graph G. Let the number of vertices in G be $2n$. (The assumption that G has even number of vertices will not affect the general validity of our results.) The subgraph obtained by deletion of the vertex r from G is denoted by G-r. Hence, G-r has $2n-1$ vertices. Of course, G-r is the graph-theoretical description of the σ complex with the sp^3 carbon atom at position r [5].

Let $P(G, x)$ be the characteristic polynomial of G and $x_1 \geqslant x_2 \geqslant \cdots \geqslant x_{2n}$ its roots. The x_j's are called the eigenvalues of the graph G [4]. The eigenvalues of the subgraph G-r will be denoted by $y_1 \geqslant y_2 \geqslant \cdots \geqslant y_{2n-1}$.

If the molecule is alternant, the corresponding molecular graph is bipartite. According to the pairing theorem [6], the bipartite graphs have the property that for all $j=1$ to n,

$$x_j + x_{2n+1-j} = y_j + y_{2n-j} = 0 \tag{1}$$

Therefore it is $x_n \geqslant 0 \geqslant x_{n+1}$ and $y_{n-1} \geqslant y_n = 0 \geqslant y_{n+1}$.

In the present paper only alternant hydrocarbons will be considered.

We introduce now an important topological function V as [7]

$$V = V(x) = i \cdot P(G\text{-}r, ix)/P(G, ix)$$

with $i = \sqrt{-1}$. As a consequence of Eq. (1), if G is bipartite, then V is real for all real values of the variable x. Moreover, it is $V(-x) = -V(x)$. Further elementary properties of the function V can be found in [7].

In terms of the function V the reactivity indices N_r, L_r and π_{rr} can be expressed as follows.

$$N_r = \langle 1 - xV \rangle \tag{2}$$

$$L_r = -\langle \log xV \rangle \tag{3}$$

$$\pi_{rr} = \langle V^2 \rangle \tag{4}$$

where we have used the abbreviate notation

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

2. Bounds for N_r, L_r and π_{rr}

The integral formulas (2), (3) and (4) were first given by Coulson in [8], [9] and [10], respectively. They will be the starting point for estimating the reactivity indices. In order to do this, we shall need certain inequalities for the function V.

First Inequality for V

Let x_1 and x_n be the largest and the smallest non-negative eigenvalue of a bipartite graph G. Then for $x \geqslant 0$,

$$x/(x^2+x_1^2) \leqslant V(x) \leqslant x/(x^2+x_n^2) \tag{5}$$

Proof. According to the pairing theorem (1), $V(x)$ of a bipartite graph can be transformed into

$$V(x) = \frac{x(x^2+y_1^2)(x^2+y_2^2)\ldots(x^2+y_{n-1}^2)}{(x^2+x_1^2)(x^2+x_2^2)\ldots(x^2+x_{n-1}^2)(x^2+x_n^2)} \tag{6}$$

Now, the Cauchy inequalities [11, 12] relate the eigenvalues of a graph G and its subgraph G-r as

$$x_1 \geqslant y_1 \geqslant x_2 \geqslant y_2 \geqslant \cdots \geqslant x_{n-1} \geqslant y_{n-1} \geqslant x_n \geqslant \cdots$$

Therefore, for $j=1$ to $n-1$,

$$(x^2+y_j^2)/(x^2+x_j^2) \leqslant 1, \qquad (x^2+y_j^2)/(x^2+x_{j+1}^2) \geqslant 1$$

which substituted back into (6) gives the inequalities (5) straightforwardly.

Inequalities (5) can be simply transformed into

$$x_n^2/(x^2+x_n^2) \leqslant 1-xV \leqslant x_1^2/(x^2+x_1^2) \tag{7}$$

Since all the three expressions in (7) are even functions, (7) holds for all x. Therefore,

$$\langle x_n^2/(x^2+x_n^2)\rangle \leqslant \langle 1-xV\rangle \leqslant \langle x_1^2/(x^2+x_1^2)\rangle$$

The left and the right integral can be evaluated by elementary methods. Thus a lower and an upper bound for bond number results. Analogous considerations yield bounds also for localization energy and atom self-polarizability. We summarize these results in the following theorem.

Theorem 1

Let x_1 and x_n be the largest and the smallest non-negative eigenvalue of the molecular graph G of an alternant hydrocarbon. Then for any site r of this molecule, the reactivity indices N_r, L_r and π_{rr} are bounded as follows.

$$x_n \leqslant N_r \leqslant x_1$$

$$2x_n \leqslant L_r \leqslant 2x_1$$

$$(2x_1)^{-1} \leqslant \pi_{rr} \leqslant (2x_n)^{-1}$$

3. On the Problem of $N_{\max}$

For the evaluation of free valence index, a maximal possible value, $N_{\max}$, for the bond number is required. In textbooks of quantum organic chemistry it is usually assumed to be a firmly established fact that

$$N_{\max} = \sqrt{d_r} \tag{8}$$

with d_r being the number of carbon atoms adjacent to the carbon atom r. As to the author's knowledge, this has not been proved anywhere in the literature[1]. We offer now a proof of Eq. (8) valid, however, for acyclic conjugated systems only. Similar statements will be also obtained for localization energy and atom self-polarizability.

Second inequality for V

Let G be an acyclic graph. Then for $x \geqslant 0$,

$$V \geqslant x/(x^2 + d_r) \tag{9}$$

where d_r is the degree of the vertex r (i.e. the number of its first neighbours). The equality in (9) holds for stars, and only for them[2].

Proof. First we note that if G is acyclic, its characteristic polynomial can be written as [15, 16],

$$P(G, x) = \sum_{j=0}^{n} (-1)^j p(G, j) x^{2(n-j)}$$

where $p(G, j)$ is the number of ways in which j non-incident edges can be selected in G. Therefore, $V(x)$ is of the form

$$V(x) = \frac{\sum_j p(G\text{-}r, j) x^{2(n-j)-1}}{\sum_j p(G, j) x^{2(n-j)}} \tag{10}$$

The quantities $p(G, j)$ fulfil the recurrence relation [15, 16]

$$p(G, j) = p(G\text{-}e_{rs}, j) + p(G\text{-}r\text{-}s, j-1) \tag{11}$$

where e_{rs} is the edge between the vertices r and s. A repeated application of Eq. (11) gives

$$p(G, j) = p(G\text{-}r, j) + \sum_s p(G\text{-}r\text{-}s, j-1) \tag{12}$$

---

[1] Eq. (8) seems to be first suggested by Moffitt [13], but without proof. Moffitt has only demonstrated how $N_{\max}$ can be determined within the valence bond approximation. Coulson's footnote in [8] about an alleged proof of (8) seems to refer to Moffitt's paper [13]. According to [14], in a private communication Coulson claimed in 1963 to be able to deduce (8) using a contour integral formalism for bond orders. This unpublished result is likely to be lost.

[2] For the definition of a star graph see Ref. [15]. Note that the stars with 2, 3, and 4 vertices are the molecular graphs of ethylene, allyl and trimethylene-methane, respectively.

with the summation going over all the vertices s adjacent to r. Note that there are just d_r such vertices.

It is easily seen that

$$p(G\text{-}r\text{-}s, j-1) \leqslant p(G\text{-}r, j-1) \tag{13}$$

since G-r-s is a subgraph of G-r. Moreover, an equality in (13) is obtained only if the vertex s is of degree one. Substitution of (13) back into (12) gives

$$p(G, j) \leqslant p(G\text{-}r, j) + d_r\, p(G\text{-}r, j-1) \tag{14}$$

From (14) one can further conclude that

$$\begin{aligned}\sum_j p(G, j) x^{2(n-j)} &\leqslant \sum_j p(G\text{-}r, j) x^{2(n-j)} + d_r \sum_j p(G\text{-}r, j-1) x^{2(n-j)} \\ &= (x + d_r/x) \sum_j p(G\text{-}r, j) x^{2(n-j)-1}\end{aligned}$$

Combination of this latter relation with Eq. (10) gives the inequality (9).

An equality in (14), and therefore also in (9), exists only if all the vertices s adjacent to r have degree one. This, on the other hand, is possible if, and only if G is a star and r is its central vertex.

Theorem 2

Let d_r be the number of carbon atoms adjacent to the carbon atom r of an acyclic polyene. Then d_r determines an upper bound for N_r and L_r and a lower bound for π_{rr} as follows.

$$N_r \leqslant \sqrt{d_r} \tag{15a}$$

$$L_r \leqslant 2\sqrt{d_r} \tag{15b}$$

$$\pi_{rr} \geqslant (2\sqrt{d_r})^{-1} \tag{15c}$$

Proof is based on a combination of the inequality (9) with Eqs. (2–4) and is completely analogous to that of Theorem 1.

Corollary 2.1. The equality in the relations (15) holds only for ethylene ($d_r = 1$) and the central atoms in allyl ($d_r = 2$) and trimethylenemethane ($d_r = 3$).

Corollary 2.2. In acyclic polyenes $N_{\text{max}} = \sqrt{d_r}$. Moreover, there exist also a maximal possible localization energy $L_{\text{max}} = 2\sqrt{d_r}$ and a minimal possible atom self-polarizability $\pi_{\text{min}} = (2\sqrt{d_r})^{-1}$.

It is likely that the inequalities (15) hold generally. A careful analysis of the proof to Theorem 2 shows, however, that its present form can not be extended to all bipartite graphs. Similarly, the proof of Theorem 1 is essentially based on the pairing theorem and it is not simple to extend it to non-alternant hydrocarbons.

Acknowledgment. The support of the Alexander von Humboldt Foundation is gratefully acknowledged.

References

1. See, e.g., Salem, L.: Molecular orbital theory of conjugated systems. New York: Benjamin 1966
2. Burkitt, F. H., Coulson, C. A., Longuet-Higgins, H. C.: Trans. Faraday Soc. **47**, 553 (1951); Greenwood, H. H.: Trans. Faraday Soc. **48**, 585 (1952); Yvan, P.: J. Chim. Phys. **49**, 457 (1952)
3. Streitwieser, A.: Molecular orbital theory for organic chemists, §11.5. New York: Wiley 1962
4. For review on the application of graph theory in the molecular orbital theory of conjugated molecules see: Gutman, I., Trinajstić, N.: Topics Curr. Chem. **42**, 49 (1973)
5. Wilcox, C. F., Gutman, I., Trinajstić, N.: Tetrahedron **31**, 147 (1975)
6. Coulson, C. A., Rushbrooke, G. S.: Proc. Cambridge Phil. Soc. **36**, 193 (1940)
7. Gutman, I., Bosanac, S.: Chem. Phys. Letters **43**, 371 (1976)
8. Coulson, C. A.: J. Chim. Phys. **45**, 243 (1948)
9. Coulson, C. A.: J. Chem. Soc. 3111 (1954)
10. Coulson, C. A., Longuet-Higgins, H. C.: Proc. Roy. Soc. (London) **A191**, 39 (1947)
11. Gutman, I.: Chem. Phys. Letters **26**, 85 (1974)
12. Dixon, W. T.: J. C. S. Faraday II **72**, 282 (1976); **73**, 67 (1977); Gutman, I., Trinajstić, N.: **73**, 435 (1977)
13. Moffitt, W. E.: Trans. Faraday Soc. **45**, 373 (1949)
14. Ref. [1], p. 293
15. Gutman, I.: Theoret. Chim. Acta (Berl.) **45**, 79 (1977)
16. Hosoya, H.: Theoret. Chim. Acta (Berl.) **25**, 215 (1972)

Received July 21, 1977