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On Structural Factors Causing Stability Differences Between Conjugated Isomers*

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The difference in total pi-electron energy of two conjugated isomers can be expressed as the integral $\langle W(x) \rangle$ of the function $W(x)$ have been determined. The main conclusion of this study bining analytical and numerical methods various properties of $W(x)$ have been determined. The main conclusion of this study is that the value of $\langle W(x) \rangle$ is determined grossly by $W(0)$, namely that algebraic structure count is the unique factor by which the relative stability of isomers is governed. In such a way the basic postulate of resonance theory has been justified.

INTRODUCTION

Recent topological studies on the total pi-electron energy (E) of conjugated hydrocarbons¹⁻³ ensured abundant information about its dependence on molecular structure. However, a closely related problem, namely the question which structural factors cause stability differences between conjugated isomers has, not yet been completely solved. This is mainly due to the fact that the approximate expressions available for E , although accurate for reproducing E , are not sufficiently accurate for reproducing the energy differences⁴. On the other hand, there exists an exact integral expression for this energy difference,

$$E(A) - E(B) = \langle W(x) \rangle \quad (1)$$

where

$$W(x) = \log \left| \frac{P(G_A, ix)}{P(G_B, ix)} \right| \quad (2)$$

G_A and G_B are molecular graphs⁵ representing two isomeric systems A and B , $P(G_A, x)$ and $P(G_B, x)$ are the corresponding characteristic polynomials⁵ and $i = \sqrt{-1}$. The derivation of eq (1) in a slightly different terminology is given in ref 6. The abbreviate notation

$$\frac{1}{\pi} \int_{-\infty}^{\infty} F(x) dx \equiv \langle F(x) \rangle \quad (3)$$

was introduced in ref 7.

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Eq (1) provides a functional dependence between $E(A) - E(B)$ and the characteristic polynomials of the two molecular graphs G_A and G_B . Furthermore, the relations between these polynomials (i. e. their coefficients) and the molecular structure are now completely understood⁸.

For reasons of mathematical simplicity, let us restrict our considerations to the alternant hydrocarbons with $2N$ conjugated atoms. A detailed analysis has shown that the final conclusions of this paper hold true for arbitrary conjugated molecules, including non-alternant and heteroconjugated systems. Further, we assume that $P(G_A, 0) \neq 0$ and $P(G_B, 0) \neq 0$, i. e. that no non-bonding pi-molecular orbitals are present in A and B , since these are necessary conditions for A and B being chemically well defined compounds⁹. Then we can write

$$P(G_A, x) = \sum_{j=0}^N (-1)^j a_j x^{2N-2j} \quad (4a)$$

$$P(G_B, x) = \sum_{j=0}^N (-1)^j b_j x^{2N-2j} \quad (4b)$$

where $a_0 = b_0 = 1$ and $a_N \neq 0$, $b_N \neq 0$. It can be shown² that for alternant hydrocarbons the coefficients, when defined as in eqs (4), obey $a_j \geq 0$, $b_j \geq 0$ for all $j = 1, \dots, N$. By substituting the formulas (4) back into (2) we get

$$W(x) = \log(A/B) \quad (5)$$

where

$$A = A(x) = x^{2N} + a_1 x^{2N-2} + a_2 x^{2N-4} + \dots + a_N \quad (6a)$$

$$B = B(x) = x^{2N} + b_1 x^{2N-2} + b_2 x^{2N-4} + \dots + b_N \quad (6b)$$

From eqs (1), (5) and (6) one can see that the difference in pi-electron energy between two isomers is a rather complicated (but analytically well defined) function of all a_j 's and b_j 's that is of the molecular structure. Therefore, although eq (1) contains all the topological information about $E(A) - E(B)$, this cannot be straightforwardly deduced from it. In the present paper we will show the most important properties of the function $W(x)$. Because of the large number of parameters which determine $W(x)$, both analytical and numerical investigations were required.

ANALYTICAL PROPERTIES OF $W(x)$

Coefficients a_1 and b_1 are equal to the number of C—C bonds in the molecules A and B , respectively⁸. Hence, from the fact that A and B are isomers it follows that $a_1 = b_1$. Let further assume that $a_j = b_j$ for $j = 1, \dots, n-1$ and $a_n \neq b_n$. Molecules A and B will be always chosen in such a manner that $a_n > b_n$. Then by dividing polynomial $A(x)$ by $B(x)$ one obtains

$$\frac{A(x)}{B(x)} = 1 + \frac{a_n - b_n}{x^{2n}} + O\left(\frac{1}{x^{2n+2}}\right) \quad (7)$$

Therefore for large $|x|$

$$W(x) \sim \log\left(1 + \frac{a_n - b_n}{x^{2n}}\right) \sim \frac{a_n - b_n}{x^{2n}} \quad (8)$$

By taking into account that $a_N \neq 0$, $b_N \neq 0$, it follows from eq (5),

$$W(0) = \log \frac{a_N}{b_N} \quad (9a)$$

$$W'(0) = 0 \quad (9b)$$

$$W''(0) = \frac{a_{N-1}}{a_N} - \frac{b_{N-1}}{b_N} \quad (9c)$$

Hence function $W(x)$ is extremal for $x = 0$. Whether this is a maximum ($W'' < 0$) or a minimum ($W'' > 0$), depends on a balance of the four coefficients a_{N-1} , a_N , b_{N-1} , b_N (eq (9c)). Since $A(x) > 0$ and $B(x) > 0$ for all x , $W(x)$ is a continuous and smooth function and we can simply conclude the following.

(a) $W(x)$ is an even function; therefore it is sufficient to analyse it in the interval $(0, \infty)$.

(b) If W has a maximum for $x = 0$, because of (8) there are additional k maxima and k minima of $W(x)$ in interval $(0, \infty)$, where $0 \leq k \leq N - 1$.

(c) If W has a minimum for $x = 0$, there are additional $k + 1$ maxima and k minima in interval $(0, \infty)$, where $0 \leq k \leq N - 1$.

The actual value of k depends in a rather complicated way on all a_j 's and b_j 's.

Up to this moment it has been tacitly assumed that all coefficients are mutually independent. However, this is by no means the case, since any a_j refer to the *same* molecule A and reflects its topological properties^{8,10}. The same is, of course, valid for b_j 's.

The (hidden) dependences between coefficients a_j (and b_j) result in additional properties of $W(x)$. Some of these properties can be established by a numerical analysis which is exposed in the next section.

NUMERICAL WORK

The idea behind the present numerical analysis is the following. Let us construct the function $W(x)$, corresponding to a particular pair of isomers A and B . We wish now to study the changes in $W(x)$ which arise when coefficient a_N is monotonically decreased while a_n is left constant. However, if we vary a_N , we must vary also a_{N-1} , a_{N-2} , \dots , since these coefficients should not be changed independently. We have chosen the following model: the variation of a_j is proportional to difference $a_j - b_j$ and decreases linearly when j changes from N to n ; the coefficients a_j for $j \leq n$ are thus left constant. In other words, $a_j(d) = a_j - d_j \cdot d$, with

$$d_j = \frac{(j-n)(a_j - b_j)}{(N-n)(a_N - b_N)} \quad (10)$$

In this way we have only one independent parameter d . We write:

$$W(x, d) = \log [A(d)/B] \quad (11)$$

where

$$A(d) = \sum_{j=0}^N a_j(d) x^{2N-2j} = A - d \sum_{j=n+1}^N d_j x^{2N-2j} \quad (12)$$

Figure 1 presents a characteristic example of a family of $W(x, d)$ functions for $A = \text{phenanthrene}$, $B = \text{anthracene}$ and $d = 0, 3, 6, 9, 12, 15$ and 18 . The form of these functions covers all cases which actually appear in chemical considerations, provided that $a_N \neq 0$ and $b_N \neq 0$. By inspection of Figure 1 conclusions (d) — (h) follow. Our numerical experience suggests that (d) — (h) are generally valid for all molecular systems without non-bonding pi-electron levels.

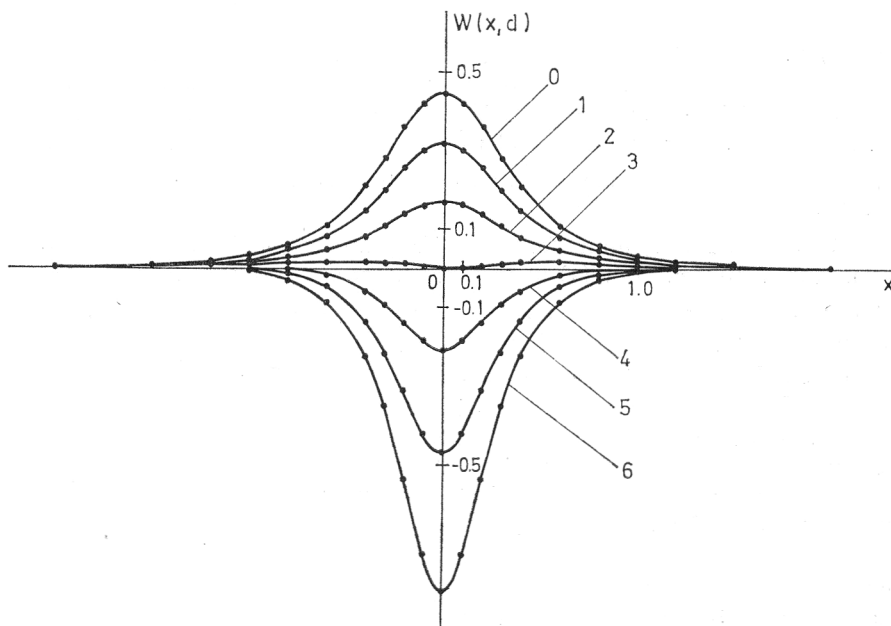


Figure 1. A family of $W(x, d)$ functions for $A = \text{phenanthrene}$, $P(G_A, x) = x^{14} - 16x^{12} + 98x^{10} - 297x^8 + 479x^6 - 407x^4 + 166x^2 - 25$, and $B = \text{anthracene}$, $P(G_B, x) = x^{14} - 16x^{12} + 98x^{10} - 296x^8 + 473x^6 - 392x^4 + 148x^2 - 16$. Curves 0, 1, 2, 3, 4, 5 and 6 correspond to $d = 0, 3, 6, 9, 12, 15$ and 18 , respectively.

(d) In all cases of chemical interest, $k = 0$. Hence (b) and (c) can be now reformulated in a more precise form.

(e) If $a_N > b_N$, the function W is maximal for $x = 0$ and monotonically decreases in interval $(0, \infty)$. If, however, $a_N/b_N \approx 1$, $W(x)$ may have also a minimum for $x = 0$, but then $\langle W(x) \rangle \approx 0$, as will be shown in (g).

(f) If $a_N \leq b_N$, $W(x)$ is minimal for $x = 0$ and has besides only one more extreme (a maximum) in $(0, \infty)$. This maximum is rather shallow since its position is shifted towards the large values of x .

(g) If $a_N = b_N$ or $a_N/b_N \approx 1$, function $W(x)$ has very small values in the whole interval $(0, \infty)$. Therefore, $\langle W(x) \rangle \approx 0$.

(h) In all cases $W(x)$ rapidly converges to zero with increasing x (c. f. eq (8)).

As a consequence of (h), large values of x give negligible contributions to $\langle W(x) \rangle$. For instance, the integration over intervals $(-\infty, -1.5)$ and $(1.5, \infty)$ contributes to the total value of $E(\text{phenanthrene}) - E(\text{anthracene})$

only by 0.005β . Accordingly, the greatest contribution to $\langle W(x) \rangle$ comes from integration over the interval of x around the zero point.

Thus we have reached our final conclusions

(i) the value of $E(A) - E(B)$ is grossly determined solely by $W(0) = \log(a_N/b_N)$, while all other coefficients a_j, b_j have a second order influence.

DISCUSSION

The chemical interpretation of conclusion (i) is based on the well known¹² fact that there is a close algebraic relation between a_N and the Kekulé structures of A . In the case of alternant hydrocarbons,

$$a_N = [\text{ASC}(A)]^2, \quad b_N = [\text{ASC}(B)]^2 \quad (13)$$

where ASC denotes the algebraic structure count¹³. Hence,

$$W(0) = 2 \log \frac{\text{ASC}(A)}{\text{ASC}(B)} \quad (14)$$

and we see that the main topological factor which causes stability differences between conjugated isomers is the difference in their algebraic structure count. The larger the ASC, the larger the predicted stability.

This, on the other hand, coincides with one of the basic concepts of resonance theory¹⁴, namely that $\text{ASC}(A) > \text{ASC}(B)$ implies $E(A) > E(B)$. The recent findings^{15,16} that resonance energy (another measure of stability) is simply a linear function of $\log \text{ASC}$, which has been interpreted¹⁵ as a »come-back« of the resonance theory, is in accord with the results of our study.

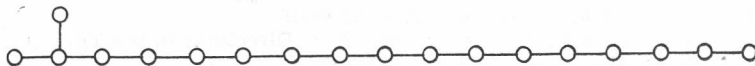
Throughout the present discussion we have not conjectured any definitive functional dependence of $E(A) - E(B)$ on $W(0)$. In the first approximation one can, of course, assume a linear relationship

$$E(A) - E(B) = C W(0) \quad (15)$$

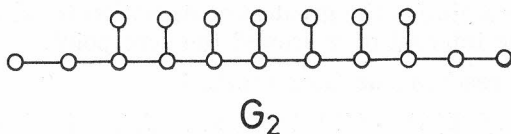
with C being a constant. But eq (15) combined with eq (14), in fact reproduces the result obtained earlier in ref 3 using a completely different way of reasoning.

Although ASC is the dominant topological factor determining the relative stability of isomers, other factors may sometimes have also a non-negligible effect. In the previous section we have found that the contributions of large values of x to integral $\langle W(x) \rangle$ are rather small. This is, however, true only if n is large and $a_n - b_n$ is small.

It is known¹⁷ that there exist pairs of isomers for which both inequalities $\text{ASC}(A) < \text{ASC}(B)$ and $E(A) > E(B)$ are fulfilled simultaneously. Therefore such isomers violate the resonance theory. The smallest possible pair of such »exceptional« structures are the two $C_{18}H_{20}$ isomers¹⁷, the molecular graphs of which are G_1 and G_2 .



G_1



For these graphs $n = 2$, $a_2 - b_2 = 6$ and thus the violation of resonance theory can be ascribed to those topological factors which effect coefficients a_2 and b_2 . It is known¹⁸ that $a_2 - b_2$ will be large if the extent of branching of A and B is considerably different. In graphs G_1 and G_2 this is evidently the case, namely while G_1 has just one branching point, and G_2 has 7 such points.

For isomers usually occurring in the chemistry of conjugated systems, the extent of branching hardly ever differs so drastically. Therefore, either $n > 2$ or $a_n - b_n$ is small (or both). For instance, in the case of the phenanthrene-anthracene pair, which we have studied, $n = 4$ and $a_4 - b_4 = 1$. Consequently, violations of the resonance theory are of a small or no practical importance, and in the vast majority of cases, considerations based solely on ASC give correct predictions.

This conclusion should be slightly changed in the case of non-alternant and heteroconjugated molecules. For those systems a_N is also related to Kekulé structures, but in a much more complicated manner^{19,20}. Then instead of eq (14) one has to use eq (9a) and to determine a_N and b_N by the graphical method developed by Wilcox¹⁹.

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SAŽETAK

O strukturnim činocima koji uzrokuju razlike u stabilnosti konjugiranih izomera

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Razlika ukupne π -elektronske energije za dva konjugirana izomera daje se izraziti integralom $\langle W(x) \rangle$ funkcije $W(x)$, čija smo svojstva odredili korištenjem analitičkih i numeričkih postupaka. Kao glavni zaključak slijedi da je integral $\langle W(x) \rangle$ uglavnom određen sa $W(0)$, naime da je račun algebarskih struktura glavni činilac koji ravna relativnom stabilnošću izomera. Na ovaj način opravdan je temeljni postulat teorije rezonancije.

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