

# Proof of Kruszewski's Rule

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A rule for the stability of isomeric polycyclic conjugated compounds, which was recently formulated by Kruszewski [1], is proved.

Kruszewski [1] recently examined how the stability of a conjugated compound is changed after addition of a new ring. He concluded that the stability of the newly formed compound depends upon the kind of bond to which the ring is attached and proposed the following rule.

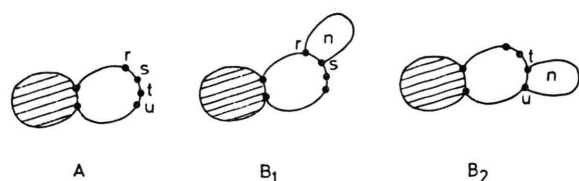
(a) If a benzene ring is attached to a conjugated system, then the greater is the  $\pi$ -electron bond order, the higher is the stability of the obtained product.

(b) If a cyclobutadiene ring is attached to a conjugated system, then the situation is reverse: the lower is the bond order, the higher is the stability of the obtained product.

Kruszewski arrived at the above rule by comparing the results of quantum chemical computations on a large number of examples. In the present paper we shall demonstrate the general validity of this regularity at least on the level of the topological theory of conjugated molecules [2].

In order to formulate Kruszewski's rule in a more precise manner, we need the following notation. Let  $A$  be a conjugated system presented by its molecular graph [2] which will also be denoted by  $A$ . Then the atom  $r$  of the molecule  $A$  is represented by a vertex  $v_r$  of the molecular graph; the bond  $rs$  is represented by an edge  $e_{rs}$ , connecting the vertices  $v_r$  and  $v_s$  [2].

We shall assume that it is possible to annelate a new  $n$ -membered ring to  $A$  either in the position  $r$ ,



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or in the position  $t, u$ ; the bonds  $rs$  and  $tu$  should not be equivalent and thus the annelation should result in two isomers:  $B_1$  and  $B_2$ .

The sites  $r, s, t, u$  belong to the same ring of the molecule  $A$ . Note that it can happen that  $s = t$ . (For concrete examples of molecules  $A, B_1$  and  $B_2$  see [1]. Kruszewski has considered the cases  $n = 6$  and  $n = 4$ .)

Let  $p_{rs}$  and  $p_{tu}$  denote the Coulson bond orders of the bonds,  $rs$  and  $tu$ , respectively, in the molecule  $A$ . Let  $E(B_1)$  and  $E(B_2)$  be the total  $\pi$ -electron energies of  $B_1$  and  $B_2$ , respectively. Then we shall prove the following proposition. Let  $m$  be an integer.

(a') If  $n = 4m + 2$ , then

$$p_{rs} > p_{tu} \Leftrightarrow E(B_1) > E(B_2)$$

(b') If  $n = 4m$ , then

$$p_{rs} > p_{tu} \Leftrightarrow E(B_1) < E(B_2)$$

where (a') holds for all  $m = 1, 2, \dots$ , whereas (b') holds at least for  $m = 1$ .

Kruszewski's rule was in fact formulated for resonance energies rather than for total  $\pi$ -electron energies. However, since  $B_1$  and  $B_2$  are isomers, the difference between their resonance energies is just equal to the difference between their total  $\pi$ -electron energies. Thus for  $m = 1$ , the statements (a') and (b') are equivalent with (a) and (b).

We shall prove (a') and (b') within the Hückel molecular orbital model. But before doing this it is instructive to show that simple resonance theoretical arguments also lead to the same conclusion.

Let the molecule  $A$  possess  $K(A)$  Kekulé structures and let among them be  $K^+(A)$  even and  $K^-(A)$  odd structures [2–4]. Then

$$K(A) = K^+(A) + K^-(A)$$

and

$$ASC(A) = K^+(A) - K^-(A),$$

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where  $ASC$  denotes the algebraic structure count [2, 3, 5]. The number of Kekulé structures of  $A$  for which the bond  $rs$  is single is  $K(A - e_{rs})$ , while the number of those Kekulé structures for which the bond  $rs$  is double is  $K(A - v_r - v_s)$ . Thus

$$K(A) = K(A - e_{rs}) + K(A - v_r - v_s)$$

Similarly,

$$K^+(A) = K^+(A - e_{rs}) + K^+(A - v_r - v_s),$$

$$K^-(A) = K^-(A - e_{rs}) + K^-(A - v_r - v_s).$$

Now, if a new  $n$ -membered ring is annelated to the bond  $rs$ , then the newly formed molecule  $B_1$  has  $K(A - e_{rs}) + 2K(A - v_r - v_s)$  Kekulé structures. If  $n = 4m + 2$ , then

$$K^+(B_1) = K^+(A - e_{rs}) + 2K^+(A - v_r - v_s),$$

$$K^-(B_1) = K^-(A - e_{rs}) + 2K^-(A - v_r - v_s),$$

and consequently

$$ASC(B_1) = ASC(A) + ASC(A - v_r - v_s).$$

Having in mind that  $ASC(A - v_r - v_s)/ASC(A)$  is the resonance theoretical bond order  $p_{rs}^{RT}$  of the bond  $rs$  in the molecule  $A$  [6], the latter equation may be rewritten as

$$ASC(B_1) = (1 + p_{rs}^{RT}) ASC(A)$$

or

$$ASC(B_1)/ASC(B_2) = (1 + p_{rs}^{RT})/(1 + p_{tu}^{RT}). \quad (1)$$

If  $n = 4m$ , then

$$K^+(B_1) = K^+(A - e_{rs}) + K^+(A - v_r - v_s) + K^-(A - v_r - v_s),$$

$$K^-(B_1) = K^-(A - e_{rs}) + K^-(A - v_r - v_s) + K^+(A - v_r - v_s),$$

and an analogous way of reasoning yields

$$ASC(B_1)/ASC(B_2) = (1 - p_{rs}^{RT})/(1 - p_{tu}^{RT}). \quad (2)$$

It has been established elsewhere [7, 8] that the difference in the stability of two conjugated isomers is, in the first approximation, proportional to the difference between the logarithms of their algebraic structure counts. Therefore (1) and (2) present a resonance theoretical justification of Kruszewski's rule.

We proceed now to prove the validity of (a') and (b') within the framework of the Hückel approximation. We shall restrict our considerations to the case when  $A$  (and therefore also  $B_1$  and  $B_2$ ) are alternant systems.

Let  $2N$  be the number of vertices and  $\Phi(A, x)$  the characteristic polynomial of the molecular graph  $A$  [2]. Let  $(A)$  denote the polynomial

$$(-1)^N \Phi(A, ix) = |\Phi(A, ix)|.$$

Since  $A$  is alternant,  $(A)$  can be presented as

$$x^{2N} + b_1 x^{2N-2} + b_2 x^{2N-4} + \cdots + b_N,$$

and the coefficients  $b_1, b_2, \dots, b_N$  are positive (or zero). Therefore  $(A)$  is positive for all real values of  $x$  (except for  $x = 0$ , where  $(A)$  may be equal to zero).

Let  $\langle f \rangle$  symbolize the integral  $\frac{1}{\pi} \int_{-\infty}^{+\infty} f(x) dx$ . Then the Coulson bond order of the bond  $rs$  of the molecule  $A$  can be presented by the expression [9, 10]

$$p_{rs} = \langle (A - v_r - v_s) / (A) \rangle - \sum_Z (-1)^{|Z|/2} \langle (A - Z) / (A) \rangle,$$

where  $Z$  denotes a  $|Z|$ -membered cycle of the molecular graph  $A$ , and the summation goes over all cycles which contain the edge  $e_{rs}$ . Since the sites  $r, s, t, u$  belong to the same ring of  $A$ , every cycle which contains  $e_{rs}$  must contain also  $e_{tu}$  and vice versa.

Therefore

$$p_{tu} = \langle (A - v_t - v_u) / (A) \rangle - \sum_Z (-1)^{|Z|/2} \langle (A - Z) / (A) \rangle$$

and

$$p_{rs} - p_{tu} = \langle (A - v_r - v_s) / (A) \rangle - \langle (A - v_t - v_u) / (A) \rangle.$$

Thus we see that the difference  $p_{rs} - p_{tu}$  is a monotonically increasing function of  $(A - v_r - v_s)$  and a monotonically decreasing function of  $(A - v_t - v_u)$ .

The difference between the total  $\pi$ -electron energies of  $B_1$  and  $B_2$  is given by [8, 11]

$$E(B_1) - E(B_2) = \langle \log[(B_1)/(B_2)] \rangle, \quad (3)$$

where

$$(B_1) = |\Phi(B_1, ix)|, \quad (B_2) = |\Phi(B_2, ix)|.$$

If  $G$  is an arbitrary bipartite graph and  $(G) = |\Phi(G, ix)|$ , then [10]

$$(G) = (G - e_{rs}) + (G - v_r - v_s) - 2 \sum_Z (-1)^{|Z|/2} (G - Z) \quad (4)$$

with the summation going over all cycles  $Z$  of  $G$  which contain the edge  $e_{rs}$ . The application of (4) to the graphs  $B_1$  and  $B_2$  gives

$$\begin{aligned}(B_1) &= (B_1 - e_{rs}) + (A - v_r - v_s) \cdot (P_{n-2}) \\ &\quad - 2 \sum_Z (-1)^{|Z|/2} (A - Z) (P_{n-2}) \\ &\quad - 2(-1)^{n/2} (A - v_r - v_s), \\ (B_2) &= (B_2 - e_{tu}) + (A - v_t - v_u) (P_{n-2}) \\ &\quad - 2 \sum_Z (-1)^{|Z|/2} (A - Z) (P_{n-2}) \\ &\quad - 2(-1)^{n/2} (A - v_t - v_u)\end{aligned}$$

with  $P_{n-2}$  denoting the path with  $n-2$  vertices. According to the construction of the molecular graphs  $B_1$  and  $B_2$ , both subgraphs  $B_1 - e_{rs}$  and  $B_2 - e_{tu}$  are mutually equal and therefore also  $(B_1 - e_{rs}) = (B_2 - e_{tu})$ .

If we denote

$$(B_1 - e_{rs}) - 2 \sum_Z (-1)^{|Z|/2} (A - Z) (P_{n-2})$$

by  $Q_n$  and

$$(P_{n-2}) - 2(-1)^{n/2} \text{ by } R_n,$$

then

$$E(B_1) - E(B_2) = \left\langle \log \frac{Q_n + R_n(A - v_r - v_s)}{Q_n + R_n(A - v_t - v_u)} \right\rangle. \quad (5)$$

One should note that  $Q_n + R_n(A - v_r - v_s) = (B_1)$  and  $Q_n + R_n(A - v_t - v_u) = (B_2)$  and thus these quantities are necessarily positive. It can also be shown that  $Q_n$  is positive for all (non-zero) values of  $x$ .

If  $n = 4m + 2$ , then the term  $R_n = (P_{n-2}) + 2$  is positive for all values of  $x$  and it follows that  $E(B_1) - E(B_2)$  is a monotonically increasing function of  $(A - v_r - v_s)$  and a monotonically decreasing function of  $(A - v_t - v_u)$ .

Combining this result with the analogous finding for  $p_{rs} - p_{tu}$ , we reach our statement (a').

Let us now examine the less simple case when  $n = 4m$ . Then the sign of the term  $R_n = (P_{n-2}) - 2$  is different for different values of  $x$  and no general regularity for the dependence of  $E(B_1) - E(B_2)$  on  $(A - v_r - v_s)$  and  $(A - v_t - v_u)$  can be deduced.

It is easy to see that  $R_n$  must be negative for small (near zero) values of  $x$  and positive for large values of  $x$ . Calculation gives

$$\begin{aligned}R_4 &< 0 \text{ for } |x| < 1.0000 \\ \text{and } R_4 &> 0 \text{ for } |x| > 1.0000, \\ R_8 &< 0 \text{ for } |x| < 0.3846 \\ \text{and } R_8 &> 0 \text{ for } |x| > 0.3846, \\ R_{12} &< 0 \text{ for } |x| < 0.2415 \\ \text{and } R_{12} &> 0 \text{ for } |x| > 0.2415, \\ R_{16} &< 0 \text{ for } |x| < 0.1764 \\ \text{and } R_{16} &> 0 \text{ for } |x| > 0.1764,\end{aligned}$$

etc.

On the other hand it has been established [8] that the gross part of an integral of type (3) comes from the integration over the near zero values of the variable  $x$  (say  $|x| < 0.5$ ). Consequently, the gross part of the integral (5) will also be determined by the near zero values of  $x$ , for which  $R_n$  is negative. Thus at least for  $n = 4$  the following conclusion is true.  $E(B_1) - E(B_2)$  is a monotonically decreasing function of  $(A - v_r - v_s)$  and a monotonically increasing function of  $(A - v_t - v_u)$ .

Therefore the result (b') is valid at least for  $m = 1$ .

This completes our proof of the Kruszewski's rule.

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