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HOSOYA INDEX OF FUSED MOLECULES

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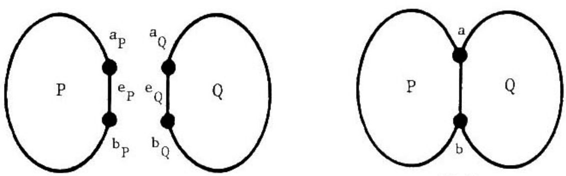
Abstract: If P and Q are two molecular graphs, then the fused system P:Q is obtained by identifying an edge of P with an edge of Q. An expression for the Hosoya index of P:Q is deduced. Also some generalizations are offered, revealing the relation between the formula for the Hosoya index of P:Q and the previously known formula for the number of Kekulé structures of P:Q.

INTRODUCTION

Two molecular graphs P and Q are said to be fused and to form a compound system P:Q if they share an edge.

Thus, let the molecular graph X (X = P, Q) possess two adjacent vertices a_X and b_X, joined by the edge e_X. Then P:Q is obtained by identifying the vertices a_P and b_P with a_Q and b_Q, respectively, i.e. by identifying the edges e_P and e_Q.



In the present paper we show that the Hosoya index of P:Q satisfies the identity

$$Z\{P:Q\} = Z\{P\}Z\{Q_{ab}\} + Z\{P_{ab}\}Z\{Q\} + Z\{P_a\}Z\{Q_b\} + Z\{P_b\}Z\{Q_a\}$$
$$- Z\{P_{ab}\}(Z\{Q_a\} + Z\{Q_b\}) - Z\{Q_{ab}\}(Z\{P_a\} + Z\{P_b\}) \quad (1)$$

where for $X = P$, Q, we use the shorthand notation X_a, X_b and X_{ab} instead of $X - a_X$, $X - b_X$ and $X - a_X - b_X$.

For the definition of the Hosoya topological index Z, its basic mathematical properties and chemical applications see Chapter 11 of the book [1]. For the present study only the following relations for Z will be needed:

$$Z\{G\} = Z\{G - e_{uv}\} + Z\{G - u - v\} \quad (2)$$

where e_{uv} symbolizes an edge of the graph G joining the vertices u and v, and

$$Z\{G_1 \cup G_2\} = Z\{G_1\}Z\{G_2\} \quad (3)$$

where $G_1 \cup G_2$ denotes a graph composed of two disconnected components G_1 and G_2.

It is worth mentioning that fully analogous relations hold for the number of Kekulé structures, viz.

$$K\{G\} = K\{G - e_{uv}\} + K\{G - u - v\} \quad (4)$$

$$K\{G_1 \cup G_2\} = K\{G_1\}K\{G_2\} \quad (5)$$

Therefore a great deal of the considerations which follow apply to both Z and K, as well as to any other topological index which conforms to relations of the type (2),(3) or (4),(5). In order to stress this we introduce the index I, such that

$$I\{G\} = I\{G - e_{uv}\} + I\{G - u - v\} \quad (6)$$

$$I\{G_1 \cup G_2\} = I\{G_1\}I\{G_2\} \quad (7)$$

Then I may be interpreted as Z or K or some other pertinent topological quantity.

A LEMMA FOR THE INDEX I

Let u be a vertex of the graph G, and let $v_1, v_2, \ldots, v_\gamma$ be the first neighbours of u. Let further the edge joining u with v_j be denoted by e_j, and $E = \{e_j | j = 1, 2, \ldots, \gamma\}$. Then applying Eq. (6) successively to $e_1, e_2, \ldots, e_\gamma$ one obtains

$$I\{G\} = I\{G - E\} + \sum_{j=1}^{\gamma} I\{G - u - v_j\}$$

where G - E is the graph obtained from G by deleting all the edges e_1, e_2, ..., e_γ.

Since in G - E the vertex u is disconnected from the rest of the system, we have G - E = (G - u)US where S symbolizes the single-vertex graph (containing just the vertex u). Because of (7) one has

$$I\{G\} = \sigma\, I\{G - u\} + \sum_{j=1}^{\gamma} I\{G - u - v_j\} \tag{8}$$

where σ stands for I{S}.

For the following considerations it is crucial to observe that for the Hosoya index σ=1 whereas for the Kekulé structure count σ=0.

A FORMULA FOR I{P:Q}

Let the vertex a_p of P be adjacent to the vertices b_p and a_i, i = 1, 2, ..., α. Let the vertex b_p of P be adjacent to the vertices a_p and b_j, j = 1, 2, ..., β. Let the edge between a_p and a_i be denoted by e_{ai}, i = 1, 2, ..., α whereas the edge between b_p and b_j by e_{bj}, j = 1, 2, ..., β. Define further the sets $E_a = \{e_{ai} | i = 1, 2, ..., \alpha\}$ and $E_b = \{e_{bj} | j = 1, 2, ..., \beta\}$.

Then the application of (6) consecutively to the edges from E_a and E_b results in

$$I\{P:Q\} = I\{P:Q - E_a - E_b\} + \sum_{i=1}^{\alpha} I\{P:Q - a - a_i - E_b\}$$
$$+ \sum_{j=1}^{\beta} I\{P:Q - E_a - b - b_j\} + \sum_{i=1}^{\alpha}\sum_{j=1}^{\beta} I\{P:Q - a - a_i - b - b_j\}$$

Bearing in mind the structure of P:Q, it can be concluded that

$$P:Q - E_a - E_b = P_{ab} \cup Q$$

$$P:Q - a - a_i - E_b = P_{aa_ib} \cup Q_a$$

$$P:Q - E_a - b - b_j = P_{abb_j} \cup Q_b$$

$$P:Q - a - a_i - b - b_j = P_{aa_ibb_j} \cup Q_{ab}$$

where $P_{aa_i b}$, P_{abb_j} and $P_{aa_i bb_j}$ stand for $P_{ab} - a_i$, $P_{ab} - b_j$ and $P_{ab} - a_i - b_j$, respectively. Then because of (7),

$$I\{P:Q\} = I\{P_{ab}\}I\{Q\} + I\{Q_a\}\sum_{i=1}^{\alpha} I\{P_{aa_i b}\} + I\{Q_b\}\sum_{j=1}^{\beta} I\{P_{abb_j}\} + I\{Q_{ab}\}\sum_{i=1}^{\alpha}\sum_{j=1}^{\beta} I\{P_{aa_i bb_j}\}$$

As special cases of the identity (8) we have

$$I\{P_b\} = \sigma\, I\{P_{ab}\} + \sum_{i=1}^{\alpha} I\{P_{aa_i b}\}$$

$$I\{P_a\} = \sigma\, I\{P_{ab}\} + \sum_{j=1}^{\beta} I\{P_{abb_j}\}$$

and

$$I\{P_{aa_i}\} = \sigma\, I\{P_{aa_i b}\} + \sum_{j=1}^{\beta} I\{P_{aa_i bb_j}\}$$

This enables one to simplify the above expression for $I\{P:Q\}$ as

$$I\{P:Q\} = I\{P_{ab}\}\, I\{Q\} + I\{P_a\}I\{Q_b\} + I\{P_b\}\, I\{Q_a\} - \sigma\, I\{P_{ab}\}(I\{Q_a\} + I\{Q_b\}) + I\{Q_{ab}\}\sum_{i=1}^{\alpha}(I\{P_{aa_i}\} - \sigma\, I\{P_{aa_i b}\}) \tag{9}$$

A further application of (8) yields

$$I\{P\} = \sigma\, I\{P_a\} + I\{P_{ab}\} + \sum_{i=1}^{\alpha} I\{P_{aa_i}\}$$

and consequently the only remaining summation on the right-hand side of (9) is transformed as

$$\sum_{i=1}^{\alpha}(I\{P_{aa_i}\} - \sigma\, I\{P_{aa_i b}\}) = I\{P\} - \sigma\, I\{P_a\} - I\{P_{ab}\} - \sigma(I\{P_b\} - \sigma\, I\{P_{ab}\}) = I\{P\} - \sigma(I\{P_a\} + I\{P_b\}) + (\sigma^2 - 1)I\{P_{ab}\}$$

This finally gives

$$I\{P:Q\} = I\{P\}I\{Q_{ab}\} + I\{P_{ab}\}I\{Q\} + (\sigma^2 - 1)I\{P_{ab}\}I\{Q_{ab}\} + I\{P_a\}I\{Q_b\} + I\{P_b\}I\{Q_a\} - \sigma\, I\{P_{ab}\}(I\{Q_a\} + I\{Q_b\}) - \sigma\, I\{Q_{ab}\}(I\{P_a\} + I\{P_b\}) \tag{10}$$

Formula (1) is an immediate special case of (10), obtained by setting I=Z and $\sigma=1$.

Note that

$$I\{P\}I\{Q_{ab}\} + I\{P_{ab}\}I\{Q\} - I\{P_{ab}\}I\{Q_{ab}\} = I\{P\}I\{Q\} - I\{P - e_P\}I\{Q - e_Q\}$$

which can be easily verified by means of (6).

Whence, Eq. (10) can be written also in the form:

$$I\{P:Q\} = I\{P\}I\{Q\} - I\{P - e_P\}I\{Q - e_Q\} + \sigma^2 I\{P_{ab}\}I\{Q_{ab}\} + I\{P_a\}I\{Q_b\}$$
$$+ I\{P_b\}I\{Q_a\} - \sigma\, I\{P_{ab}\}(I\{Q_a\} + I\{Q_b\}) - \sigma\, I\{Q_{ab}\}(I\{P_a\} + I\{P_b\}) \quad (11)$$

DISCUSSION

Setting I=K and $\sigma=0$ into Eq. (11) one obtains the formula

$$K\{P:Q\} = K\{P\}K\{Q\} - K\{P - e_P\}K\{Q - e_Q\} + K\{P_a\}K\{Q_b\} + K\{P_b\}K\{Q_a\}$$

Since $K\{G\} \neq 0$ only if G has even number of vertices, we can distinguish between the cases when

(a) P and Q are even systems:

$$K\{P:Q\} = K\{P\}K\{Q\} - K\{P - e_P\}K\{Q - e_Q\};$$

(b) P and Q are odd systems:

$$K\{P:Q\} = K\{P_a\}K\{Q_b\} + K\{P_b\}K\{Q_a\};$$

(c) P is even and Q is odd or vice versa:

$$K\{P:Q\} = 0.$$

The above expressions for $K\{P:Q\}$ have been reported previously [2].

Denote by (P:Q)* the molecular graph obtained by identifying the vertices a_P and b_P of P with the vertices b_Q and a_Q of Q, respectively. If neither P possesses a plane of symmetry passing through e_P nor Q possesses a plane of symmetry passing through e_Q, then the systems P:Q and (P:Q)* are not mutually isomorphic.

From (10) we straightforwardly obtain

$$I\{(P:Q)^*\} - I\{P:Q\} = (I\{P_a\} - I\{P_b\})(I\{Q_a\} - I\{Q_b\}) \quad (12)$$

Further, if P and Q are identical (and are identically labeled), then

$$I\{(P:P)^*\} - I\{P:P\} = (I\{P_a\} - I\{P_b\})^2 \quad (13)$$

We see that if I is a real-valued quantity, then irrespectively of the nature of the topological index I, the difference I{(P:P)*} - I{P:P} is non-negative and is strictly positive if $I\{P_a\} \neq I\{P_b\}$. Note that this latter inequality implies that $P_a \neq P_b$ and therefore $(P:P)^* \neq P:P$.

Eqs. (12) and (13) are to some extent analogous to certain relations in the theory of TEMO [3, 4], which hold for the characteristic polynomials of the so-called S- and T-isomers. In fact, the systems P:Q and (P:Q)* can be understood as a certain pair of S,T-isomers.

However, since no molecular-orbital-energy-like quantities can be associated with the topological index I, we deem that the above indicated analogy with TEMO is formal and needs not have any physical implications.

In the case I = K (number of Kekulé structures), the relation (13) was reported in an earlier work [5]. In the case I = Z (Hosoya index), the relations (12) and (13) seem not to have been observed previously.

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[2] S.J. Cyvin, B.N. Cyvin and I. Gutman, Z. Naturforsch. 42a, 181 (1987).

[3] For the theory of the topological effect on molecular orbitals (TEMO) see: O.E. Polansky, G. Mark and M. Zander, Der topologische Effekt an Molekülorbitalen (TEMO) - Grundlagen und Nachweis, MPI für Strahlenchemie, Mülheim 1987, and the references cited therein.

[4] The present Eqs. (12) and (13) should be compared with Eqs. (8) and (9), respectively, from Chapter 4 of the book [3].

[5] I. Gutman, O.E. Polansky and M. Zander, Match 15, 145 (1984).