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**A MATHEMATICAL MODEL OF THE *SYNTHON*\***

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*Dedicated to the memory of Prof. M. Sekanina.*

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A mathematical model of the *synthon* is suggested. The term *synthon* is used to denote one or several molecules or their part(s) with free valences. The notion of isomeric synthons on a set of atoms  $A$  and that of the *Family of Isomeric Synthons*  $FIS(A)$  are introduced. Matrix operators are defined for modelling the elementary steps of reorganization of electrons during reactions. A new notion of the reaction distance of isomeric *synthons* is introduced as the smallest number of elementary steps of reorganization of electrons during the reaction transforming one *synthon* into another.

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Recently we concerned ourselves with a formal study of electronic processes at monatomic reaction centres<sup>1</sup> (valence states of atoms) and at diatomic reaction centres<sup>2</sup> (atomic vectors). Although this concept enables the majority of the decisive so-called elementary steps of reorganization of electrons during chemical reactions to be treated, it is not amenable to all steps. Formally, all steps of reorganization of valence electrons can be treated by applying elementary matrix operators, as are included in the ASSOR program<sup>3</sup> and constitute a part of the algebraic model of constitutional chemistry<sup>4</sup>. An alternative approach consists of the use of elementary reaction graph operators<sup>5</sup> within the graph model of constitutional chemistry<sup>6,7</sup>. The two models allow for the description of the topological structure of a molecule and of the global electronic phenomena occurring during a reaction. However, relying on a stoichiometric basis and requiring conservation of the global number of valence electrons within the systems, the models do not enable us to flexibly treat part of molecules (reaction centres). Their applicability is additionally reduced by the fact that the modelling of the elementary electronic processes in them rests to a high degree on a combinatorial basis. Although these shortcomings do not detract from the wide use of these models in chemistry, they have stimulated the setting up of a novel model that may be more flexible in relation to the deductive planning

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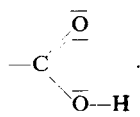
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of organic syntheses in both the forward and backward directions and to proposals of reaction mechanisms. This model is the subject of the present work.

### *Mathematical Model of Synthons and Their Reactions*

The fundamental concept underlying the model in question, which is also one of the primary concepts in theoretical considerations of the synthesizing chemist, is the generalized concept of the *synthon*. In its original sense<sup>8</sup>, the *synthon* is understood as that part of the substrate at which some change occurs during the chemical reaction of interest. In our model, the *synthon* is one or more whole molecules or a part of a molecule. The structure of the *synthon* is built up on a fixed set of atoms  $A$ , denoted symbolically as  $S(A)$ . This concept has been derived from that of an ensemble of molecules  $EM(A)$ , used<sup>4,9</sup> for the set of summary formulae of one or several molecules constructed from atoms of set  $A$ . Against the definition of  $EM(A)$ ,  $S(A)$  is extended in that it may involve free valences, i.e. bonds that do not connect two atoms but which only start from an atom. Such bonds are construed as bonds between a particular real atom of the *synthon* and a free, so-called virtual, atom, which is not specified. The concept of virtual atoms adds appreciably to the deductive power of the model, various concrete atoms or groups being conceived in place of a virtual atom in particular cases.

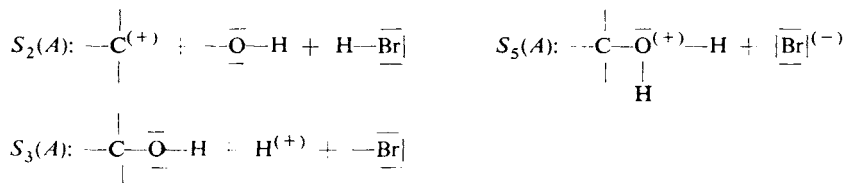
*Example 1.* A synthon  $S(A)$  on a set of atoms  $A = \{C, O, O, H\}$  is, for instance, the structure



Two synthons  $S(A)$ ,  $S(B)$  are said to be isomeric if they are defined on the same set of atoms, hence, if  $A = B$ . The set of all isomeric *synthons* built on a set  $A$  will be referred to as a *Family of Isomeric Synthons* and denoted  $FIS(A)$ , in analogy with  $FIEM(A)$  built up<sup>4,9</sup> as a set of all isomeric  $EM(A)$ . In our model the definition of isomerism is looser because it does not require conservation of the global number of valence electrons, thereby enabling also nonstoichiometric processes to be modelled. The formal study of the constitution chemistry of a set of atoms  $A$  reduces to a study of  $FIS(A)$ . The fundamental notion of the model is that of the valence state of an atom<sup>1,9-13</sup>.

*Example 2.* For  $A = \{C, O, H, H, Br\}$ , the following structures are *synthons*  $S_1(A)$  through  $S_5(A)$  included in  $FIS(A)$ :





### Matrix Model of Synthon

Formally, a *synthon*  $S(A)$  on a set of atoms  $A = \{A_1, A_2, \dots, A_n\}$  is characterized by the number and kind of atoms involved and by the localization of chemical bonds and lone valence electrons between the atoms and at the atoms. Thus the chemical constitution expressed by the electronic formula is subject to treatment.

Mathematically, a *synthon* is expressed by the so-called *synthon BE-matrix* (SBE, henceforth referred to as the S-matrix),  $\mathbf{M} = (m_{ij})$ , which off the main diagonal is defined as the BE-matrix<sup>4,9</sup> and the  $m_{ii}$  elements are the four-component vectors of the valence states of the atoms<sup>1,9,11</sup>  $A_i$ . It is clear that  $\mathbf{M}$  is a symmetric square matrix of rank  $n$ . The headings of the rows and columns contain the individual atoms from set  $A$ .

*Example 3.* The S-matrix of the *synthon*  $S_1(A)$  from Example 2 is

	C	O	H	H	Br
C	(0, 4, 0, 0)	1	0	0	0
O	1	(4, 2, 0, 0)	1	0	0
H	0	1	(0, 1, 0, 0)	0	0
H	0	0	0	(0, 1, 0, 0)	1
Br	0	0	0	1	(6, 1, 0, 0)

It is often convenient to work with a part of the *synthon*  $S(A)$  only, a so-called *subsynthon*, which will be defined as follows. Given a *synthon*  $S(A)$  on set  $A$  and a *synthon*  $S(X)$  on set  $X$ , with S-matrices  $\mathbf{M}$  and  $\mathbf{M}'$ , respectively, we say that *synthon*  $S(X)$  is a *subsynthon* of *synthon*  $S(A)$  if

1.  $X$  is a subset of set  $A$ ,
2.  $\mathbf{M}'$  is a submatrix of matrix  $\mathbf{M}$ .

*Example 4.* Consider sets  $A = \{\text{C, O, H, H, Br}\}$ ,  $X = \{\text{C, O}\}$  and *synthons*

$S_1(A)$  from Example 2 and its S-matrix from Example 3,  $S_1(X) = \begin{array}{c} | \\ \text{---C---}\overline{\text{O}}\text{---} \\ | \end{array}$  and its S-matrix

C	(0, 4, 0, 0)	1
O	1	(4, 2, 0, 0)

$S'(X) = \text{>C}^{(+)}\text{—}\overline{\text{O}}$  and its  $S$ -matrix

$$\begin{array}{cccc} \text{C} & (0, 3, 0, 0) & & 1 \\ \text{O} & & 1 & (4, 2, 0, 0) \end{array}$$

Now, *synthon*  $S_1(X)$  is a *subsynthon* of *synthon*  $S_1(A)$  whereas *synthon*  $S'(X)$  is not, the  $S$ -matrix of the latter being no submatrix of the  $S$ -matrix of *synthon*  $S_1(A)$ .

It is clear from the definition of the *subsynthon* as well as from Example 4 that the property of "being a *subsynthon*" preserves the valence states of all atoms with respect to the initial *synthon*.  $S(X)$  being a *subsynthon* of *synthon*  $S(A)$  will be denoted  $S(X) \subset S(A)$ .

### Matrix Model of Reactions of Synthon

The underlying principle of this model is the fact that a chemical reaction is a process during which reorganization of bonds and lone valence electrons takes place. This process is described by the so-called *synthon reaction matrix* ( $SR$ -matrix), which is an analogy of the  $R$ -matrix<sup>4,9,13</sup> or the  $R$ -graph<sup>5</sup>. The  $SR$ -matrix is defined for each pair of *synthons*  $S(A)$ ,  $S'(A)$  belonging to a  $FIS(A)$ . For the reaction  $S(A) \rightarrow S'(A)$  the  $SR$ -matrix,  $\mathbf{P}$ , is defined as

$$\mathbf{P} = \mathbf{M}' - \mathbf{M}, \quad (1)$$

where  $\mathbf{M}$  and  $\mathbf{M}'$  are the  $S$ -matrices of the two *synthons*, respectively. This operation of subtraction consists of subtraction of matrices for the off-diagonal elements and subtraction of vectors for the main diagonal elements.

*Example 5.* Consider the reaction  $S(A) \rightarrow S'(A)$  for *synthons*  $S(A) = \text{H—}\overline{\text{C}}\text{—}$   
 $\text{—}\overline{\text{C}}\text{—}\overline{\text{Br}}$  and  $S'(A) = \text{H—}\overline{\text{Br}}$  +  $\text{>C}=\text{C}<$ . The  $SR$ -matrix for the corresponding change,  $\mathbf{P}$ , is

$$\begin{array}{l} \text{H} \\ \text{C} \\ \text{C} \\ \text{Br} \end{array} \left| \begin{array}{cccc} (0, 1, 0, 0) & 0 & 0 & 1 \\ 0 & (0, 2, 1, 0) & 2 & 0 \\ 0 & 2 & (0, 2, 1, 0) & 0 \\ 1 & 0 & 0 & (6, 1, 0, 0) \end{array} \right| -$$

$$- \left| \begin{array}{cccc} (0, 1, 0, 0) & 1 & 0 & 0 \\ 1 & (0, 4, 0, 0) & 1 & 0 \\ 0 & 1 & (0, 4, 0, 0) & 1 \\ 0 & 0 & 1 & (6, 1, 0, 0) \end{array} \right| =$$

$$= \begin{vmatrix} (0, 0, 0, 0) & -1 & 0 & 1 \\ -1 & (0, -2, 1, 0) & 1 & 0 \\ 0 & 1 & (0, -2, 1, 0) & -1 \\ 1 & 0 & -1 & (0, 0, 0, 0) \end{vmatrix}.$$

It is clear that emerging from subtraction of two symmetric matrices, the *SR*-matrix is symmetric. In contrast to the *R*-matrix, the sum of all elements of the *SR*-matrix need not be equal to zero.

The chemical reaction is represented in the model by the matrix equation

$$\mathbf{M} + \mathbf{P} = \mathbf{M}' \quad (2)$$

which is directly derived from Eq. (1); here  $\mathbf{M}$  and  $\mathbf{M}'$  are the *S*-matrices of the educts and products, respectively,  $\mathbf{P}$  is the corresponding *SR*-matrix.

### Elementary Conversions of Synthons

Now, concentrate on the elementary electronic processes at a *synthon*. The concept is based on the treatment of elementary processes of reorganization of electrons<sup>1,11,12</sup> and the definition of the elementary electronic processes in the ASSOR program<sup>3</sup>. Four types of elementary matrix operators are introduced for modelling the elementary electronic processes.

1. Operator  $\alpha_k^{ij}$  for the electrofugal (from the viewpoint of the *i*-th atom) dissociation of bond between the *i*-th and *j*-th atoms, and operator  $-\alpha_k^{ij}$  for association of the same kind; *k* denotes the multiplicity of the bond concerned.

2. Operator  $\beta_k^{ij}$  for the nucleofugal (from the viewpoint of the *i*-th atom) dissociation of bond between the *i*-th and *j*-th atoms, and operator  $-\beta_k^{ij}$  for association of the same kind. It is clear that  $\beta_k^{ij} = \alpha_k^{ji}$  ( $i \neq j$ ).

3. Operator  $\gamma_k^{ij}$  for the homolysis of bond between the *i*-th and *j*-th atoms, and  $-\gamma_k^{ij}$  for association of the radicals.

4. Operators  $\delta_l^{ij}$  and  $-\delta_l^{ij}$  for redox processes associated with the oxidation and reduction, respectively, of the *i*-th atom; here  $l = 1$  or  $2$  according to the number of electrons exchanged.

Operators  $\alpha_k^{ii}$ ,  $-\alpha_k^{ii}$ ;  $\beta_k^{ii}$ ,  $-\beta_k^{ii}$ ;  $\gamma_k^{ii}$ ,  $-\gamma_k^{ii}$ ; and  $\delta_l^{ii}$ ,  $-\delta_l^{ii}$  refer to situations where a virtual atom is involved instead of the *j*-th atom. The concrete forms of the operators are given in Table I.

Matrix representation of the elementary operators is matrices of the same kind as the *SR*-matrices; the application of the elementary operators is accomplished by matrix addition according to Eq. (2) where  $\mathbf{P}$  is the corresponding elementary matrix operator from Table I.

TABLE I

Matrix form of elementary operators. All elements that are not given explicitly are zeroes;  
 $\beta_k^{ij} = \alpha_k^{ji}$

Operator	Matrix and process modelled		
	$k = 1$	$k = 2$	$k = 3$
$\alpha_k^{ij}$	$\begin{array}{ccc} & i & j \\ & \vdots & \vdots \\ i \dots & (2, -1, 0, 0) \dots & -1 \\ & \vdots & \vdots \\ j \dots & -1 \dots & (0, -1, 0, 0) \dots \\ & \vdots & \vdots \\ & \text{I} \rightarrow \text{J} & \rightarrow \bar{\text{I}} \rightarrow \text{J} \end{array}$	$\begin{array}{ccc} & i & j \\ & \vdots & \vdots \\ \dots & (2, 1, -1, 0) \dots & -1 \\ & \vdots & \vdots \\ \dots & -1 \dots & (0, 1, -1, 0) \dots \\ & \vdots & \vdots \\ & \text{I} \rightarrow \text{J} & \rightarrow \bar{\text{I}} \rightarrow \text{J} \end{array}$	$\begin{array}{ccc} & i & j \\ & \vdots & \vdots \\ \dots & (2, 0, 1, -1) \dots & -1 \\ & \vdots & \vdots \\ \dots & -1 \dots & (0, 0, 1, -1) \dots \\ & \vdots & \vdots \\ & \text{I} \rightarrow \text{J} & \rightarrow \bar{\text{I}} \rightarrow \text{J} \end{array}$
$\alpha_k^{ii}$	$\begin{array}{c} i \\ \vdots \\ i \dots (2, -1, 0, 0) \dots \\ \text{I} \rightarrow \text{I} \end{array}$	$\begin{array}{c} i \\ \vdots \\ \dots (2, 1, -1, 0) \dots \\ \text{I} \rightarrow \bar{\text{I}} \end{array}$	$\begin{array}{c} i \\ \vdots \\ \dots (2, 0, 1, -1) \dots \\ \bar{\text{I}} \rightarrow \bar{\text{I}} \end{array}$
$\beta_k^{ii}$	$\begin{array}{c} i \\ \vdots \\ i \dots (0, -1, 0, 0) \dots \\ \text{I} \rightarrow \bar{\text{I}} \end{array}$	$\begin{array}{c} i \\ \vdots \\ \dots (0, 1, -1, 0) \dots \\ \text{I} \rightarrow \bar{\text{I}} \end{array}$	$\begin{array}{c} i \\ \vdots \\ \dots (0, 0, 1, -1) \dots \\ \text{I} \rightarrow \bar{\text{I}} \end{array}$
$\gamma_k^{ij}$	$\begin{array}{ccc} & i & j \\ & \vdots & \vdots \\ i \dots & (1, -1, 0, 0) \dots & -1 \dots \\ & \vdots & \vdots \\ j \dots & -1 \dots & (1, -1, 0, 0) \dots \\ & \vdots & \vdots \\ & \text{I} \rightarrow \text{J} & \rightarrow \text{I}' \rightarrow \text{J}' \end{array}$	$\begin{array}{ccc} & i & j \\ & \vdots & \vdots \\ \dots & (1, 1, -1, 0) \dots & -1 \dots \\ & \vdots & \vdots \\ \dots & -1 \dots & (1, 1, -1, 0) \dots \\ & \vdots & \vdots \\ & \text{I} \rightarrow \text{J} & \rightarrow \text{I}' \rightarrow \text{J}' \end{array}$	$\begin{array}{ccc} & i & j \\ & \vdots & \vdots \\ \dots & (1, 0, 1, -1) \dots & -1 \\ & \vdots & \vdots \\ \dots & -1 \dots & (1, 0, 1, -1) \dots \\ & \vdots & \vdots \\ & \text{I} \rightarrow \text{J} & \rightarrow \text{I}' \rightarrow \text{J}' \end{array}$
$\gamma_k^{ii}$	$\begin{array}{c} i \\ \vdots \\ i \dots (1, -1, 0, 0) \dots \\ \text{I} \rightarrow \text{I}' \end{array}$	$\begin{array}{c} i \\ \vdots \\ \dots (1, 1, -1, 0) \dots \\ \text{I} \rightarrow \text{I}' \end{array}$	$\begin{array}{c} i \\ \vdots \\ \dots (1, 0, 1, -1) \dots \\ \text{I} \rightarrow \text{I}' \end{array}$
$\delta_1^{ij^a}$	$\begin{array}{ccc} & i & j \\ & \vdots & \vdots \\ i \dots & (-1, 0, 0, 0) \dots & 0 \\ & \vdots & \vdots \\ j \dots & 0 \dots & (1, 0, 0, 0) \dots \\ & \vdots & \vdots \\ & \text{I}' \rightarrow \text{J} & \rightarrow \text{I}' \rightarrow \text{J}' \end{array}$	$\begin{array}{ccc} & i & j \\ & \vdots & \vdots \\ \dots & (-2, 0, 0, 0) \dots & 0 \\ & \vdots & \vdots \\ \dots & 0 \dots & (2, 0, 0, 0) \dots \\ & \vdots & \vdots \\ & \text{I}' \rightarrow \text{J} & \rightarrow \text{I}' \rightarrow \text{J}' \end{array}$	—
$\delta_1^{ii^a}$	$\begin{array}{c} i \\ \vdots \\ i \dots (-1, 0, 0, 0) \dots \\ \text{I}' \rightarrow \text{I} \end{array}$	$\begin{array}{c} i \\ \vdots \\ \dots (-2, 0, 0, 0) \dots \\ \bar{\text{I}} \rightarrow \text{I} \end{array}$	—

<sup>a</sup>  $k$  is replaced by  $l$  in the heading.

*Example 6.* By application of operator  $\alpha_1^{4,3}$  to *synthon*  $S(A)$  from Example 5 we obtain matrix  $\mathbf{P}$ :

$$\begin{array}{l} \text{H} \\ \text{C} \\ \text{C} \\ \text{Br} \end{array} \left| \begin{array}{cccc} (0, 1, 0, 0) & 1 & 0 & 0 \\ 1 & (0, 4, 0, 0) & 1 & 0 \\ 0 & 1 & (0, 4, 0, 0) & 1 \\ 0 & 0 & 1 & (6, 1, 0, 0) \end{array} \right| + \\ + \left| \begin{array}{cccc} (0, 0, 0, 0) & 0 & 0 & 0 \\ 0 & (0, 0, 0, 0) & 0 & 0 \\ 0 & 0 & (0, -1, 0, 0) & -1 \\ 0 & 0 & -1 & (2, -1, 0, 0) \end{array} \right| = \\ = \left| \begin{array}{cccc} (0, 1, 0, 0) & 1 & 0 & 0 \\ 1 & (0, 4, 0, 0) & 1 & 0 \\ 0 & 1 & (0, 3, 0, 0) & 0 \\ 0 & 0 & 0 & (8, 0, 0, 0) \end{array} \right|$$

Chemically interpreted,  $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overline{\text{Br}} \rightarrow \text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}^{(+)} + \overline{\text{Br}}^{(-)}$ . So, the first step of elimination or substitution proceeding by the monomolecular mechanism is obtained.

#### Isomeric Synthons and the $FIS(A)$ Graph Concept

It will be convenient for practical applications to model the set  $FIS(A)$  by the so-called  $FIS(A)$  graph, denoted  $G_{FIS(A)}$  and defined in terms of the ordered pair  $V, E$  as

$$G_{FIS(A)} = (V, E), \quad (3)$$

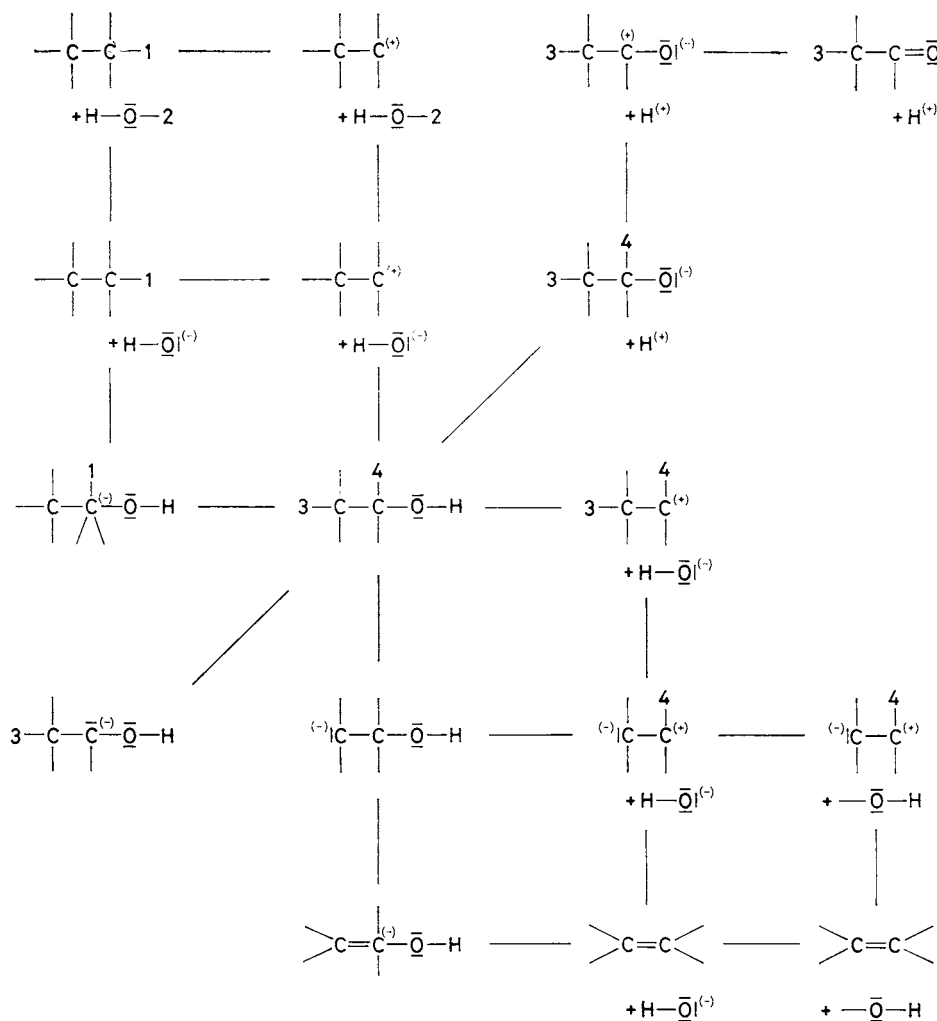
where  $V$  is the set of all *synthons* belonging to  $FIS(A)$  and  $E$  is the set of unoriented edges. An edge exists between vertices  $x$  and  $y$  if an elementary conversion transforming *synthon*  $x$  into *synthon*  $y$  exists; hence,

$$V = \{v_1, v_2, \dots, v_n \mid v_i \in FIS(A)\} \quad (4)$$

$$E = \{\{x, y\} \mid x, y \in V \wedge \exists \circ \in O \text{ such that } \mathbf{M} + \circ = \mathbf{M}'\}, \quad (5)$$

where  $O$  is the set of elementary operators defined in Table I and  $\mathbf{M}$  and  $\mathbf{M}'$  are matrices of *synthons*  $x$  and  $y$ , respectively.

A part of the graph  $G_{FIS(A)}$  for  $A = \{\text{C}, \text{C}, \text{O}, \text{H}\}$  is shown in Scheme 1. The entire graph, even for diatomic *synthons*, contains too many vertices to lend itself



SCHEME 1

A section of the graph  $G_{FIS(A)}$  for  $A = \{C, C, O, H\}$ . The numbers label formally some virtual vertices to make for a good observation of changes on them if any

to graphical presentation. The lower estimate of the number of vertices in the graph  $F_{FIS(A)}$  for *synthons* on various sets is given in Table II. Subgraphs of graph  $G_{FIS(A)}$  are sufficient for practical applications; they can be of use particularly for examining the precursors and synthetic successors of a *synthon* during synthesis and reaction mechanisms. Reaction mechanisms are treated as time-ordered successions of elementary steps of electron reorganizations<sup>14</sup>, represented by paths in the graph



$G_{FIS(A)}$ . In the subgraph in Scheme 1, for instance, the paths modelling the  $S_N1$  and  $S_N2$  mechanisms on the *subsynthon*  $\begin{array}{c} | \\ -C-\bar{O}-H \\ | \end{array}$  or the E1 mechanism on the *synthon*  $\begin{array}{c} | \\ -C-C-\bar{O}-H \\ | \end{array}$  can be traced.

The graph  $G_{FIS(A)}$  is also the starting structure for the definition of a notion that is of importance in the model treated, viz that of the reaction distance.

### Reaction Distance

The concept of the reaction distance emerges from that of the chemical distance, which is the sum of absolute values of elements of the  $R$ -matrix<sup>4,9</sup> (also modified as the minimum value of this sum for various arrangements of atoms in  $BE$ -matrices of the educt and product<sup>6</sup>). Now, we introduce this new concept of the *reaction distance* ( $RD$ ) as the graph distance in the  $G_{FIS(A)}$  graph as follows. Let *synthons*  $S(A)$ ,  $S'(A)$  be elements of  $FIS(A)$  and  $x$  and  $y$ , vertices in the graph  $G_{FIS(A)}$  representing the two *synthons* respectively. Then

$$RD(S(A), S'(A)) = D(x, y), \quad (6)$$

where  $D$  is the length of the shortest path between vertices  $x$  and  $y$  in the graph  $G_{FIS(A)}$ . The graph distance being a metric on the corresponding graph<sup>15</sup> (if the phenomenological assumption of continuity of the  $F_{FIS(A)}$  graph is met), the reaction distance  $RD$  is a metric on  $FIS(A)$ .

Chemically interpreted, the reaction distance is the smallest number of elementary steps of reorganization of valence electrons during the reaction from the starting *synthon* to the final *synthon*. For instance, Scheme 1 demonstrates that if  $S_1(A)$  is

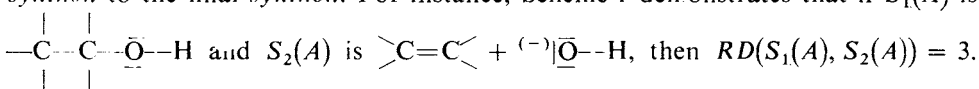


TABLE II

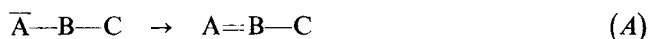
Lower estimate of number of vertices in graph  $G_{FIS(A)}$  for various sets  $A$

$A$	Lower estimate of number of vertices
$\{C\}$	35
$\{C, C\}$	1 225
$\{H, C, C\}$	7 350
$\{H, C, C, Br\}$	154 350
$\{H, C, C, C, Br\}$	5 402 250

This concept has been employed in a similar context as the minimal number of unit reactions<sup>16</sup>. In that form, however, it cannot be used, e.g., as heuristic for the study of reaction mechanisms; moreover, the algorithm of the calculation has not been given.

Generally, the concepts of the chemical distance (*CD*) and the reaction distance are not identical. The chemical distance mirrors the global number of valence electrons that "migrate" during the reaction, and it rather expresses the thermodynamic view upon the process under study. The reaction distance, on the other hand, is associated with the elementary processes of electron reorganization and concerns more the kinetic aspect of the process. The difference between the two distances is illustrated by Example 7.

*Example 7.* Consider reactions represented by the following reaction schemes:



Whereas *CD* = 4 for both reactions, *RD* = 1 for reaction (A) and *RD* = 2 for reaction (B).

The above deficiency of the chemical distance concept may be one of the reasons that the principle of minimum chemical distance<sup>17</sup> (*PMCD*) is not always accepted by the nature.

In practice the *RD* cannot be calculated from the  $G_{FIS(A)}$  graph using a computer because of the too large extent of this graph. The calculation of the *RD* is no trivial task; the treatment of this topic will be the subject of a forthcoming paper.

## CONCLUSIONS

Mathematical modelling of chemical reality is prerequisite for a number of applications, among them the computer assisted planning of organic syntheses. So far, the algebraic model by Dugundji and Ugi<sup>4</sup> and its graph analogue by Kvasnička<sup>5-7</sup> were sufficient for this purpose. The model proposed in this paper attempts to approach the viewpoint of the synthesizing chemist by introducing the concept of unoccupied (virtual) atoms, contributing to the deductive power of the model and enabling one to choose concrete atoms or groups in particular cases treated.

A next asset of the model is its ability to model in a natural manner the elementary steps of reorganization of valence electrons during chemical reactions, thereby employing another powerful weapon of the chemist-synthesist, viz. the theory of reaction mechanisms.

It is also noteworthy that the model is not combinatorial; instead, it is based on concrete valence states of atoms, described in the literature and hence, realistic.

Construing the constitutional chemistry of a set of atoms  $A$  as the chemistry of  $FIS(A)$ , it is perhaps not inappropriate to call this model an algebraic model of realistic constitutional chemistry.

*The setting up of the model suggested has been provoked by numerous discussions with Associate Professor M. Kratochvíl (Institute of Pure Chemicals, Lachema, Brno) on problems of computer aided planning of chemical syntheses and the role of mathematical models therein. Thanking Prof. M. Kratochvíl is therefore more than a pleasant duty.*

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