Description of Organic Reactions Based on Imaginary Transition Structures. 4. Three-Nodal and Four-Nodal Subgraphs for a Systematic Characterization of Reactions

SHINSAKU FUJITA

Research Laboratories, Ashigara, Fuji Photo Film Co., Ltd., Minami-Ashigara, Kanagawa, Japan 250-01

A three-nodal subgraph having a central carbon atom, e.g., A—O—C—//—B, which is abstracted from an imaginary transition structure, is a clue for perception of organic reactions. Oxidative, reductive, and isohypsic reactions can be discriminated by comparing electronegativities of the atoms A and B. A four-nodal subgraph, e.g., A—//—C—O—C—//—B or A—O—C—//—C—O—B, affords information about construction and cleavage reactions. Eliminations and addition with respect to a double bond can be perceived by such a four-nodal subgraph as A—//—C≈C—//—B or A—O—C≈C—O—B.

The recognition of organic reactions is a difficult problem open to all organic chemists who intend to put organic synthesis design (and retrieval of organic reactions) into a more systematic format. All methods proposed for description of organic reactions have been based on the methodology in which each organic reaction is recognized as structural difference between a substrate and a product.[1] This methodology implies dual expression, i.e., reference to the substrate (for the product) and to the reaction type. The duality has never been pointed out clearly as to be undesirable, and so there have been few methods that intend avoiding this difficulty. In order to overcome such duality, I have proposed the concept of imaginary transition structure (ITS) as a unitary representation of an organic reaction.[2] In the first part of this paper, I will compare several methods with the ITS concept from this viewpoint. Then, I will propose three-nodal and four-nodal subgraphs to characterize organic reactions.

COMPARISON OF THE ITS CONCEPT WITH OTHER METHODS FOR DESCRIPTION OF ORGANIC REACTION

Let us examine several representative methods using the Cope rearrangement as an example (Scheme I). Hendrickson's elaborate method[3] recognizes a reaction at one carbon site as a pair of the capital letters R, Π, H, and Z, the first indicating the attachment formed in the reaction, the second the attachment removed. In his system of codification, the Cope rearrangement is represented by a code of RΠ.ΠΠ. ΠR.ΠR.ΠΠ.RΠ. His treatment is concerned only with information of a reaction type and affords no information of an individual reaction, since the above codification discards other structural features of an individual reaction. As a result, both the structure of the substrate (or product) and the reaction type must be referred to when one wishes to describe an individual reaction.

The dual reference is also necessary in Ugi's comprehensive system,[4] in which reactants and products are denoted by B and E matrices, respectively, and a reaction is represented by R matrix ($R = E - B$). For example, the Cope rearrangement corresponds to an R matrix of Scheme I. The R matrix indicates a reaction type rather than an individual reaction. Hence, the recognition of the individual reaction needs both information of the structure of reactants and the R matrix. Moreover, the same R matrix corresponds to different reaction types such as the Diels–Alder reaction, the retro Diels–Alder reaction, the Claisen rearrangement, oxy-Cope rearrangement, trimerization of an acetylene to benzene, and so on. Therefore, they cannot be discriminated from each other by Ugi's system unless one refers to the reactants (or the products).
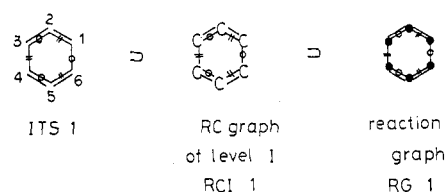
Scheme I

1) Hendrickson:[3]

2) Ugi (R matrix):[4]

3) Fujita (ITS):[2]

| ITS 1 | RC graph of level 1 RCl 1 | reaction graph RG 1 |

The ITS of a given reaction is an extended structural formula, which contains three-colored bonds, i.e., out-bonds (—//—), in-bonds (—O—), and par-bonds (—), according to the structural change during the reaction.[2,5] The ITS is a full expression of the structural change of the individual reaction and can be manipulated as a kind of structural formula. The above-described reaction (Scheme I) is represented by ITS **1**. One can extract a graph of reaction centers (RC graph) of level 1 (RC₁) and a reaction graph (RG) from the ITS (**1**) as subgraphs, both of which correspond to reaction types.

THREE-NODAL SUBGRAPHS AS CLUES FOR CLASSIFICATION OF ORGANIC REACTIONS

The RC graphs of various levels are descriptors of the reaction types as discussed in the previous papers of this series.[6] More detailed examination of ITS's is necessary for the perception of reduction or oxidation. In this section, I will discuss a three-nodal subgraph of an RC graph of level 1 (RC₁) in

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Table I. IT's, RC$_1$'s, and Three-Nodal Subgraphs of Reductions

entry	ITS	RC$_1$	three-nodal subgraph	code	ref
1			H–•–C–++–O O–≡–C–±±–N	H(0+1)C(1-1)O O(1+1)C(2-1)N	7
2			H–•–C–++–O	H(0+1)C(1-1)O	8
3			H–•–C–++–O	H(0+1)C(1-1)O	9
4			H–•–C–++–O	H(0+1)C(1-1)O	10
5			H–•–C–±–O	H(0+1)C(2-1)O	11
6			H–•–C–++–Cl	H(0+1)C(1-1)Cl	12
7			H–•–C–++–Br	H(0+1)C(1-1)Br	13
8			H–•–C–++–Br	¹H(0+1)C(1-1)Br	14
9			Mg–•–C–++–Br	Mg(0+1)C(1-1)Br	15
10			Li–•–C–++–Cl	Li(0+1)C(1-1)Br	16

order to characterize such reaction types as subdivided. Table I collects ITS's and RC$_1$'s of various reductions. When RC graphs of level 1 (Table I) are examined carefully, they involve three-nodal subgraphs, each of which has a central carbon atom and two adjacent non-carbon atoms. For example, H–O–C–//–O is extracted as a three-nodal subgraph from the RC graph of entries 1–4 and codified as H(0+1)C(1-1)O by using complex bond numbers.[5] The three-nodal subgraph of **5**$_{RC1}$ is extracted as H–O–C≡O, which holds information of par-bonds. Other types of reactions (entries 6–10) are listed in Table I. Each of the three-nodal subgraphs of Table I has a hydrogen or less electronegative atom (attached through an (*a b*) bond of *b* = 1) and a more electronegative atom (attached through an (*a b*) bond of *b* = –1) at both terminal positions. This formulation clarifies the features of reductions.

Table II shows several examples of oxidation reactions, which provide three-nodal subgraphs of reverse types as compared with reductions. The mechanism of oxidations are not

understood thoroughly, but the most plausible ITS's to my knowledge are collected in Table II.

Table III shows the classification of three-nodal subgraphs having a central carbon atom. Suppose that a three-nodal subgraph is A(a' +1)C(a –1)B, wherein A and B are selected from H and Z. Here, I use H as a hydrogen or other less electronegative atom, and Z as a more electronegative atom. When the electronegativity of atom A is greater than that of B, the reaction at the carbon site is oxidative. When A is less electronegative than B, the reaction is reductive. When A and B are equal in electronegativity, the reaction is a substitution or isohypsic reaction.

For comparison, Table III involves Hendrickson's codes,[22] which have no information of par-bonds, or, in other words, consider only *b* values of the complex bond number (*a b*). Thus, several types of reactions are designated by the same codes, e.g., ZZ, HZ, and ZH. But their reaction features are considerably different, and so they must be discriminated,

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Table II. ITS's, RC$_1$'s, and Three-Nodal Subgraph of Oxidations

entry	ITS	RC$_1$	three-nodal subgraph	code	ref
11			O⧣C⧢H	O(1+1)C(1−1)H	17
12			O⧣C⧢H	O(1+1)C(1−1)H	18
13			O⧢C⧢H	O(0+1)C(1−1)H	19
14			O⧣C⧢H	O(1+1)C(1−1)H	20
15			Br⧢C⧢H	Br(0+1)C(1−1)H	21

Table III. Types of Reactions Based on Three-Nodal Subgraphs

three-nodal subgraph	code	name of type	Hendrickson's code[a]
H⧢C⧢H	H(0+1)C(1−1)H	proton exchange	HH
Z⧢C⧢Z	Z(0+1)C(1−1)Z	nucleophilic substitution	ZZ
Z⧢C⧣Z	Z(0+1)C(2−1)Z	nucleophilic addition to a double bond	
Z⧣C⧢Z	Z(1+1)C(1−1)Z	nucleophilic elimination to form a double bond	
Z⧣C⧣Z	Z(1+1)C(2−1)Z	π-rearrangement	
Z⧢C⧤Z	Z(0+1)C(3−1)Z	nucleophilic addition to a triple bond	
Z⧤C⧢Z	Z(2+1)C(1−1)Z	nucleophilic elimination to form a triple bond	
Z⧣C⧤Z	Z(1+1)C(3−1)Z	π-rearrangement	
Z⧤C⧣Z	Z(2+1)C(2−1)Z	π-rearrangement	
Z⧢C⧢H	Z(0+1)C(1−1)H	oxidation	ZH
Z⧣C⧢H	Z(1+1)C(1−1)H	oxidative elimination to form a double bond	
Z⧤C⧢H	Z(2+1)C(1−1)H	oxidative elimination to form a triple bond	
H⧢C⧢Z	H(0+1)C(1−1)Z	reduction	HZ
H⧢C⧣Z	H(0+1)C(2−1)H	reductive addition to a double bond	
H⧢C⧤Z	H(0+1)C(3−1)H	reductive addition to a triple bond	

[a]See ref 22.

especially from the viewpoint of reaction retrieval.

FOUR-NODAL SUBGRAPHS AS CLUES FOR CLASSIFICATION OF ORGANIC REACTIONS

Four-nodal subgraphs are useful to describe reactions with respect to two carbon sites (Table IV). For example, a pinacol reduction (entry 16) is represented by ITS **16**. The corresponding four-nodal subgraph, O=C—O—C=O (or its code O(2−1)C(0+1)C(2−1)O), is a descriptor of this reaction. Since two terminal atoms are both oxygens, this reaction is classified as a reductive construction.

The second example (entry 17) claims ITS **17**. The four-nodal subgraph extracted from ITS **17** is Rh—//—C—O—C—//—I, which is codified as Rh(1−1)C(0+−1)C(1−1)I. Since rhodium is a less electronegative atom (H) and iodine is a more electronegative one (Z), this reaction is classified as an isohypsic construction. The same situations are effected in entries 18−21. The reactions of entries 22 and 23 are reductive constructions, which are denoted by four-nodal subgraphs represented by general formula Z—//—C—O—C—//—Z.

Oxidative cleavages, as exemplified in entries 24−26, are characterized by general four-node subgraph Z—O—C—//—C—O—Z which may be modified by par-bonds and in-bonds.

Entries 27 and 28 correspond to other types of C−C bond cleavages.

In general, the code A(a′ −1)C(0 +1)C(a″ −1)B is a four-nodal subgraph of construction. Contrarily, the code A(a′ +1)C(1 −1)C(a″ +1)B represents cleavage. Both types of four-nodal subgraphs are classified as oxidative, isohypsic, or reductive by comparing the electronegativities of terminal A and B atoms (Table V). It should be emphasized again that the descriptors collected in Table V appear in ITS's as subgraphs.

Table VI collects eliminations and additions with respect to C=C double bonds. The four-nodal subgraph of elimination is A—//—C=C—//—B, in general, which may be modified by par-bonds at the terminal ITS bonds and is codified as A(a′ −1)C(1 +1)C(a″ −1)B. On the other hand, additions afford A—O—C=C—O—B as a general four-nodal subgraph. The code is A(a′ + 1)C(2−1)C(a″ + 1)B. The atoms, A and B, are selected from a set of groups (H and Z) as defined above. The reactions cited in Table VI can be classified in the light of Table VII. The terms, i.e., oxidative, isohypsic, and reductive, are the same as in Table V.

Eliminations and additions with respect to C≡C triple bonds can be treated in the same line as above. The four-nodal subgraphs of elimination reactions are represented by A—//—C≡C—//—B, in general, the terminal bonds of which may

Table IV. ITS's, RC_1's, and Four-Nodal Subgraphs of Constitutions and Cleavage

entry	ITS	RC_1	four-nodal subgraph	code	ref
16			O≢C⊷C≢O	O(2–1)C(0+1)C(2–1)O	23
17			Rh⊬C⊷C⊬I	Rh(1–1)C(0+1)C(1–1)I	24
18			Mg⊬C⊷C⊬O	Mg(1–1)C(0+1)C(1–1)O	25
19			Mg⊬C⊷C⊬O	Mg(1–1)C(0+1)C(1–1)O	26
20			Mg⊬C≢C⊬O	Mg(1–1)C(0+1)C(2–1)O	27
21			Mg⊬C≢C⊬O	Mg(1–1)C(0+1)C(2–1)O	28
22			Cl⊬C⊷C⊬Br	Cl(1–1)C(0+1)C(1–1)Br	29
23			N⊬C⊷C⊬N	N(1–1)C(0+1)C(1–1)N	30
24			O≢C⊬C⊷Br	O(1+1)C(1–1)C(0+1)Br	31
25			O≢C⊬C≢O	O(1+1)C(1–1)C(1+1)O	32
26			O≢C⊬C≢O	O(1+1)C(1–1)C(1+1)O	33
27			O⊷C⊬C⊷H	O(0+1)C(1–1)C(0+1)H	34
28			B⊷C⊬C⊷H	B(0+1)C(1–1)C(0+1)H	35

be modified by single or double par-bonds. The corresponding code is A(a′ –1)C(2+1)C(a″ –1)B. The four-nodal subgraph A—O—C≡C—O—B (where said in-bonds may be modified by single and double par-bonds) or corresponding code A(a′ +1)C(3–1)C(a″ +1)B represents an addition to a triple bond. The terms oxidative, isohypsic, and reductive are also effective in these cases.

Five- or more-nodal subgraphs are also useful for characterization of organic reactions; I will discuss this point elsewhere.

It is worthy here to discuss the difference between my ITS approach and Hendrickson's system with respect to metho-

dology of perception of an organic reaction. Hendrickson's system reduces an organic reaction into a change at one carbon site, and the total feature of the reaction is represented by a set of such changes. Thus, entry 17 of Table IV is represented by RH (oxidative construction) and RZ (reductive construction), respectively, at the two carbon sites. The total reaction is denoted by RH.RZ (isohypsic construction). In this case, the total isohypsic construction is perceived as oxidative plus reductive constructions.

On the other hand, the ITS approach affords the four-nodal subgraph   Rh—//—C—O—C—//—I   (in   general, H—//—C—O—C—//—Z) for the same reaction. Then the re-

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Table V. Constructions and Cleavages Represented by Four-Nodal Subgraphs

four-nodal subgraph	code	name of type	Hendrickson's code[a]
		Constitution	
H–C–C–H	H(1–1)C(0+1)C(1–1)H	oxidative construction	RH.RH
H–C–C–Z	H(1–1)C(0+1)C(1–1)Z	isohypsic construction	RH.RZ
H–C–C–Z	H(1–1)C(0+1)C(2–1)Z	isohypsic construction (additive)	
H–C–C–Z	H(1–1)C(0+1)C(3–1)Z	isohypsic construction (additive)	
Z–C–C–Z	Z(1–1)C(0+1)C(1–1)Z	reductive construction	RZ.RZ
Z–C–C–Z	Z(1–1)C(0+1)C(2–1)Z	reductive construction (additive)	
Z–C–C–Z	Z(1–1)C(0+1)C(3–1)Z		
Z–C–C–Z	Z(2–1)C(0+1)C(2–1)Z		
Z–C–C–Z	Z(2–1)C(0+1)C(3–1)Z		
Z–C–C–Z	Z(3–1)C(0+1)C(3–1)Z		
		Cleavages	
H–C–C–H	H(0+1)C(1–1)C(0+1)H	reductive cleavage	HR.HR
H–C–C–Z	H(0+1)C(1–1)C(0+1)Z	isohypsic cleavage	HR.ZR
H–C–C–Z	H(0+1)C(1–1)C(1+1)Z	isohypsic cleavage (eliminative)	
H–C–C–Z	H(0+1)C(1–1)C(2+1)Z	isohypsic cleavage (eliminative)	
Z–C–C–Z	Z(0+1)C(1–1)C(0+1)Z	oxidative cleavage	ZR.ZR
Z–C–C–Z	Z(0+1)C(1–1)C(1+1)Z	oxidative cleavage (eliminative)	
Z–C–C–Z	Z(0+1)C(1–1)C(2+1)Z		
Z–C–C–Z	Z(1+1)C(1–1)C(1+1)Z		
Z–C–C–Z	Z(1+1)C(1–1)C(2+1)Z		
Z–C–C–Z	Z(2+1)C(1–1)C(2+1)Z		

[a] See ref 22.

**Table VI.** ITS's, RC$_1$'s, and Four-Nodal Subgraphs of Elimination and Additions
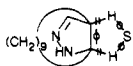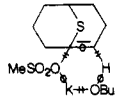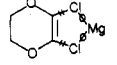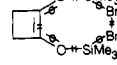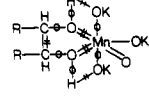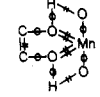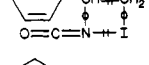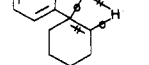
entry	ITS	RC$_1$	four-nodal subgraph	code	ref
29			H–C≡C–C–H	H(1–1)C(1+1)C(1–1)H	36
30			H–C≡C–C–O	H(1–1)C(1+1)C(1–1)O	37
31			H–C≡C–C–O	H(1–1)C(1+1)C(1–1)O	38
32			Cl–C≡C–C–Cl	Cl(1–1)C(1+1)C(1–1)Cl	39
33			O≡C≡C≡O	O(1+1)C(2–1)C(1+1)O	40
34			O–C≡C–O	O(0+1)C(2–1)C(0+1)O	41
35			Br–C≡C–Br	Br(0+1)C(2–1)C(0+1)Br	42
36			N–C≡C–I	N(0+1)C(2–1)C(0+1)I	43
37			H–C≡C–O	H(0+1)C(2–1)C(0+1)O	44
38			H–C≡C–H	H(0+1)C(2–1)C(0+1)H	45
39			H–C≡C–H	H(0+1)C(2–1)C(0+1)H	46

Table VII. Eliminations and Additions Represented by Four-Nodal Subgraphs

four-nodal subgraph	code	name of type	Hendrickson's code[a]
		Eliminations	
H—C≡C—H	H(1–1)C(1+1)C(1–1)H	oxidative elimination	ΠH.ΠH
H—C≡C—Z	H(1–1)C(1+1)C(1–1)Z	isohypsic elimination	ΠH.ΠZ
H—C≡C≡Z	H(1–1)C(1+1)C(2–1)Z	isohypsic π-rearrangement (eliminative)	
H—C≡C≡Z	H(1–1)C(1+1)C(3–1)Z	isohypsic π-rearrangement (eliminative)	
Z—C≡C—Z	Z(1–1)C(1+1)C(1–1)Z	reductive elimination	
Z—C≡C≡Z	Z(1–1)C(1+1)C(2–1)Z	reductive π-rearrangement	ΠZ.ΠZ
Z—C≡C≡Z	Z(1–1)C(1+1)C(3–1)Z		
Z≡C≡C≡Z	Z(2–1)C(1+1)C(2–1)Z		
Z≡C≡C≡Z	Z(2–1)C(1+1)C(3–1)Z		
Z≡C≡C≡Z	Z(3–1)C(1+1)C(3–1)Z		
		Additions	
H—C≡C—H	H(0+1)C(2–1)C(0+1)H	reductive addition	HΠ.HΠ
H—C≡C—Z	H(0+1)C(2–1)C(0+1)Z	isohypsic addition	HΠ.ZΠ
H—C≡C≡Z	H(0+1)C(2–1)C(1+1)Z	isohypsic π-rearrangement (additive)	
H—C≡C≡Z	H(0+1)C(2–1)C(2+1)Z	isohypsic π-rearrangement (additive)	
Z—C≡C—Z	Z(0+1)C(2–1)C(0+1)Z	oxidative addition	ZΠ.ZΠ
Z—C≡C≡Z	Z(0+1)C(2–1)C(1+1)Z	oxidative π-rearrangement (additive)	
Z—C≡C≡Z	Z(0+1)C(2–1)C(2+1)Z		
Z≡C≡C≡Z	Z(1+1)C(2–1)C(1+1)Z		
Z≡C≡C≡Z	Z(1+1)C(2–1)C(2+1)Z		
Z≡C≡C≡Z	Z(2+1)C(2–1)C(2+1)Z		

[a] See ref 22.

action feature is discerned as an isohypsic construction, wherein the term "construction" is derived from the graph C—O—C and "isohypsic" stems from the comparison of the terminal atoms (H vs. Z). As a result, Table III does not involve the counterparts of such Hendrickson's codes as RR, ΠΠ, RH, HR, RZ, ZR, RΠ, ΠR, ΠH, HΠ, ΠZ, and ZΠ, none of which exist independently in the sense of the present ITS approach.

IMAGINARY VALENCY, OUT-VALENCY, IN-VALENCY, PAR-VALENCY, AND INTRASTRING AND EXTRASTRING PAR-VALENCY

This section provides numerical correlation of the present ITS approach to Hendrickson's elaborate system. Imaginary valency (IV) is valency appearing in an ITS, which consists of out-, in-, and par-valency. I define out-valency (v_o) of an atom as the number of out-bonds incident to the atom in a given ITS. Similarly, the number of in-bonds incident to an atom is called the in-valency (v_i) of the atom. Par-valency (v_p) is the number of par-bonds, which may be par-bonds abbreviated in the ITS. The definition implies the following equation: IV = v_o + v_i + v_p. The number of adjacent atoms is called a connectivity number, which is denoted as CN. Each valency of an atom is classified as electropositive (h), electroneutral (σ), or electronegative (z) according to the nature of the adjacent atom connected by said valency. The symbol h indicates that said valency concerns an adjacent hydrogen atom or other less electronegative atom. Thus, o_h is out-valency concerning an adjacent hydrogen and so on. The subscript σ indicates that said valency links an adjacent atom of almost the same electronegativity. The symbol z is a valency to more electronegative atoms.

Par-valency is defined to be intrastring when it modifies a reaction string and to be extrastring when it is not contained in the reaction string. In the previous section, attention was focused only on intrastring par-valency. However, more precise treatment must consider extrastring par-valency. Intrastring and extrastring par-valency may construct a double or triple bond.

The parameter p_{zis} is an intrastring single par-valency, which is an electronegative character (z), p_{zed} is an extrastring double par-valency, which concerns hydrogen or less electronegative atom z, and so on. Thus, I can obtain the following set of parameters:

o_h	o_σ	o_z	
i_h	i_σ	i_z	intrastring
p_{his}	$p_{\sigma is}$	p_{zis}	
p_{hid}	$p_{\sigma id}$	p_{zid}	
p_{hes}	$p_{\sigma es}$	p_{zes}	
p_{hed}	$p_{\sigma ed}$	p_{zed}	extrastring
p_{het}	$p_{\sigma et}$	p_{zet}	

The following equations are obtained from the definition:

$$v_o = o_h + o_\sigma + o_z$$

$$v_i = i_h + i_\sigma + i_z$$

$$v_p = p_{his} + p_{\sigma is} + p_{zis} + (p_{hid} + p_{\sigma id} + p_{zid}) + (p_{hes} + p_{\sigma es} + p_{zes}) + (p_{hed} + p_{\sigma ed} + p_{zed}) + (p_{het} + p_{\sigma et} + p_{zet})$$

Hendrickson[22] defined a carbon site by its four attachments: R = σ bond to carbon (number = σ), Π = π bond to carbon (number = π), H = bond to H or other less electronegative atom (number = h), Z = bond to more electronegative atom (number = z). He classified reactions at one carbon site by the values $\Delta\sigma$, Δz, $\Delta\pi$, Δh, Δc, and Δx. His elaborate treatment will be reexamined here in the light of the present ITS approach. Hendrickson's parameters can be rewritten by the imaginary valency defined above.

$$\sigma^{(s)} = o_\sigma + (p_{\sigma is} + p_{\sigma id}) + (p_{\sigma es} + p_{\sigma ed} + p_{\sigma et})$$

$$\sigma^{(p)} = i_\sigma + (p_{\sigma is} + p_{\sigma id}) + (p_{\sigma es} + p_{\sigma ed} + p_{\sigma et})$$

$$z^{(s)} = o_z + (p_{zis} + p_{zid}) + (p_{zes} + p_{zed} + p_{zet})$$

$$z^{(p)} = i_z + (p_{zis} + p_{zid}) + (p_{zes} + p_{zed} + p_{zet})$$

$$h^{(s)} = o_h + (p_{his} + p_{hid}) + (p_{hes} + p_{hed} + p_{het})$$

$$h^{(p)} = i_h + (p_{his} + p_{hid}) + (p_{hes} + p_{hed} + p_{het})$$

$$\pi^{(s)} = 4 - (\sigma^{(s)} + z^{(s)} + h^{(s)})$$

$$\pi^{(p)} = 4 - (\sigma^{(p)} + z^{(p)} + h^{(p)})$$

$$x^{(s)} = z^{(s)} - h^{(s)}$$

$$x^{(p)} = z^{(p)} - h^{(p)}$$

Then the following expressions are obtained easily:

$$\Delta\sigma = i_\sigma - o_\sigma$$

$$\Delta z = i_z - o_z$$

$$\Delta h = i_h - o_h$$

$$\Delta\pi = (o_\sigma - i_\sigma) + (o_z - i_z) + (o_h - i_h)$$

$$\Delta c = 9(i_\sigma - o_\sigma) - (i_h - o_h)$$

$$\Delta x = (i_z - o_z) - (i_h - o_h)$$

Since the parameters of each carbon atom are obtained easily from ITS, all parameters defined by Hendrickson can be calculated by equations derived above. Thus, the present ITS approach embraces Hendrickson's method. The numerical treatment described in this section shows that Hendrickson's system discarded information about par-valency but the ITS approach holds this information. Further advantages of the ITS stem from its graphical treatment and will be discussed in the following section.

EXTRASTRING PAR-VALENCY

Further aspects of each reaction are obtained by examination of extrastring par-valency of the three-node subgraph. For example, the center carbon atom of Z—O—C—//—H implies extrastring par-valency of three.

The edge ($\sigma = 0$) of Hendrickson's character triangle[22] contains a set of carbon sites substituted by increased number of Z's. His system codifies all steps of this edge by the same code ZH, and hence, dual expression is necessary for description of each step, e.g., CH_4 (the starting stage) and ZH (the reaction) for the first step. On the other hand, ITS's of these steps are different from each other in extrastring substitutions. It should be mentioned here that all procedures for choice of descriptors of reactions are substituted by manipulation of the ITS as an extended structural formula.

Hendrickson:
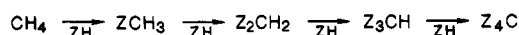
ITS (Fujita):
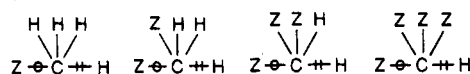
CONCLUSION

I have proposed three-nodal and four-nodal subgraphs for characterization of organic reactions. They are extracted from RC graphs of level 1, which, in turn, are the subgraphs of ITS's.

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