Similarity Ideas in the Theory of Pericyclic Reactivity

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The recently introduced similarity approach to chemical reactivity is reviewed. The examples demonstrating the broad possibilities of the so-called similarity indices in the qualitative rationalization of various mechanistic features of pericyclic reactions are discussed. The topics covered include (i) the alternative reproduction of Woodward–Hoffmann rules, (ii) the systematic investigation of the possibility of substituent-induced violation of these rules, (iii) a simple criterion allowing the discrimination between one-step and stepwise mechanisms of pericyclic processes, and (iv) the theoretical confirmation of the Evans–Dewar concept of aromaticity of transition states.

INTRODUCTION

The creation of theoretical models describing the behavior of systems is a general process accompanying the increasing exploitation of various mathematical methods and procedures in all areas of natural sciences. In contemporary chemistry, this general tendency finds its reflection in an effort at the quantitative specification of various important but originally rather intuitively introduced, notions and concepts. One of the most useful such concepts is that of molecular similarity. The scope of studies dealing with the quantitative exploitation of molecular similarity is extremely heterogeneous[1] and ranges from the attempts to characterize the similarity in molecular shape[2-6] to the application of various distance and similarity measures in the field of computer-designed synthesis.[7-9]

Parallel with these efforts there is also another group of more physically oriented papers attempting to relate the similarity in molecular properties to the similarity in the electron structure of corresponding molecules.[10-20] A typical example in this respect is the so-called similarity index.[10] Although the problem of this index and of some other related quantities is currently the subject of intensive investigations,[10-16] the majority of these studies are restricted to the simple static comparison of electron structures, especially from the point of view of the rational prediction of physical and biological properties of molecules.

The increasing use of various similarity ideas in recent years has been enriched by new interesting attempts to extend the applicability of the approach beyond the scope of static structure–activity relationships to what is the heart of chemistry—chemical reactivity. An example of this may be our recent study[20] dealing with the alternative reproduction of Woodward–Hoffmann rules.[21] This study has become the basis of a number of subsequent generalizations in which we demonstrated not only the usefulness but also the remarkable universality of the approach, allowing it to be applied in a number of various fields of pericyclic reactivity.

Our aim in this paper is to review the results of these studies and to demonstrate the broad applicability of the approach in the theory of pericyclic reactions. The paper is divided into several parts, each of which deals with one, relatively closed field of pericyclic reactivity, i.e., the alternative reproduction of Woodward–Hoffmann rules and the problem of eventual substituent induced violation of these rules. Other topics discussed are concerned with the relation of the similarity index to the so-called least motion principle,[22] the possibility of the discrimination between one-step and stepwise reaction mechanisms in pericyclic reactions, and the theoretical justification of the Evans–Dewar concept of aromaticity of transition states.

(1) SIMILARITY INDEX IN THEORY OF CHEMICAL REACTIVITY

The idea of the quantitative exploitation of molecular similarity for the classification of regularities in chemical properties is probably due to Polansky,[23] who attempted to justify theoretically Clar's old idea of local benzenoid regions in condensed aromatic hydrocarbons.[24] For this purpose, Polansky introduced a coefficient r_L, characterizing the similarity of a given local benzenoid fragment L in a molecule to the standard isolated benzene in terms of corresponding density matrices P and P_L (eq 1):

$$r_L = (1/2N_L)\mathrm{Tr}PP_L \qquad (1)$$

Because of normalization by the factor $2N_L$ (N_L is the number of electrons in a fragment L), the values of the coefficient vary between 0 and 1, measuring the extent of similarity.

More recently, the idea of quantitative comparison of electron structure of the molecules was revived by Carbo,[10] who proposed for this purpose the similarity index r_{AB} expressing the desired similarity of two isoelectronic molecules A, B in terms of density matrices (eq 2):

$$r_{AB} = \frac{\int \rho_A(1)\rho_B(1)\,d\tau}{(\int \rho_A^2(1)\,d\tau)^{1/2}(\int \rho_B^2(1)\,d\tau)^{1/2}} \qquad (2)$$

This definition has also become the basis of our generalization of the similarity index[20] directed for its use in the theory of chemical reactivity. The first step of such a generalization consists in the specification of the molecules, the similarity of which we are interested in. In this respect, the natural choice is to identify the molecules A and B with the reactant and the product of a given reaction. The original index r_{AB} thus transforms into the index r_{RP}. The next important step of the generalization is concerned with the approximations necessary for the practical calculation of the index. It appears that the direct calculation of the index by the straightforward integration of the general expression (eq 1) is not convenient. The most important drawback is concerned with the fact that the values of the index (eq 1) are not invariant to the distance and the mutual position of the corresponding molecules. Analysis

of this invariance problem has revealed that this inconvenient feature is generally caused by the presence of multicenter integrals $I_{\mu\nu\lambda\sigma}$ (eq 3):

$$I_{\mu\nu\lambda\sigma} = \int \chi_\mu^R \chi_\nu^R \chi_\lambda^P \chi_\sigma^P \, d\tau \tag{3}$$

In order to eliminate the problems with the invariance, we proposed a topological approximation based on the recently introduced overlap determinant method.[25] The basis of this approximation is the transformation matrix T, which describes the mutual-phase relation of atomic orbitals centered on molecules R and P and, thus, plays in this approach the same role as the so-called assigning tables in the overlap determinant method (eq 4):

$$\chi^P = T\chi^R \tag{4}$$

The construction of this matrix is sufficiently described in the original studies,[20,25] and, therefore, it is not necessary to repeat it here. We recall only that the form of this matrix depends on the actual reaction mechanism of the transformation R $\rightarrow$ P, so that it is just via this matrix that the possibility to discriminate between various reaction mechanisms enters into play.

Combining eq 4 with the usual ZDO-like approximation (eq 5) for multicenter integrals and the idempotency relations

$$I_{\mu\nu\alpha\beta} \cong \delta_{\mu\alpha}\delta_{\nu\beta} \tag{5}$$

(eq 6), the original definition equation (eq 2) can be rewritten

$$\sum_\mu \sum_\nu \rho_{\mu\nu}^2 = 2N \tag{6}$$

in the final form (eq 7), which can be regarded as a generalization of the original formula of Polansky. The most

$$r_{RP} = (1/2N)\mathrm{Tr}\mathbf{P}_R\bar{\mathbf{P}}_P \tag{7a}$$

$$\bar{\mathbf{P}}_P = T^{-1}\mathbf{P}_P T \tag{7b}$$

important feature of this generalization consists in the direct inclusion of the transformation matrix T with which the various reaction paths can be quantitatively distinguished.

(2) SIMILARITY INDEX AND SELECTION RULES IN CHEMICAL REACTIVITY

One of the most interesting examples of the above-mentioned possibility of discriminating between the various reaction paths is concerned with the alternative reproduction of the Woodward–Hoffmann rules.[21] This reproduction is based on simple intuitive interpretation, according to which the magnitude of r_{RP} is a quantitative measure of the extent of electron reorganization accompanying the transformation of the reactant into the product. Generally, it is natural to expect that high values of r can be regarded as indicating low electron reorganization and vice versa. Such an intuitive interpretation is especially interesting because of its relation to the so-called least motion principle,[22] according to which the reactions prefer those reaction paths along which the reacting molecules undergo minimal changes in nuclear and electron configurations of the reacting molecules. In view of the above relationship between the magnitude of r and the extent of electron reorganization, the ease of the reaction can be characterized by the value of the similarity index.

This intuitive parallel can be best demonstrated with the example of the so-called electrocyclic reactions for which the

Table I. Comparison of First- and Second-Order Similarity Indices for Several Selected Pericyclic Reactions

reaction	mechanism[a]	r_{RP}	g_{RP}
butadiene/cyclobutadiene	conrotation	0.724	0.524
	disrotation	0.500	0.091
hexatriene/cyclohexadiene	disrotation	0.759	0.566
	conrotation	0.659	0.358
ethene dimerization	s + a	0.500	0.250
	s + s	0.500	0.091
Diels–Alder reaction	s + s	0.575	0.298
	s + a	0.575	0.272
Cope rearrangement	s + s	0.500	0.206
	s + a	0.500	0.206

[a] Upper value corresponds to the allowed and the lower value corresponds to the forbidden reaction mechanism.
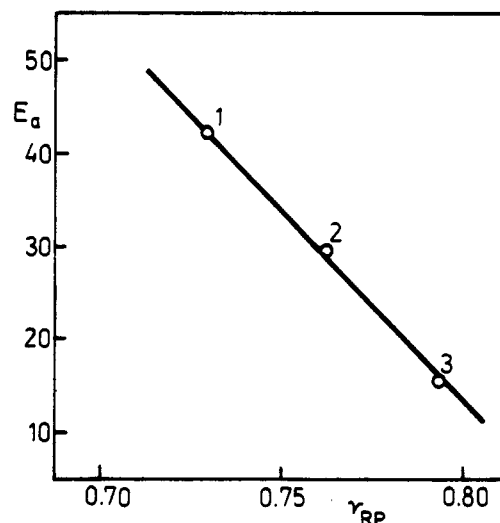

Figure 1. Empirically found correlation between the similarity indices r_{RP} and the experimental values of activation energies for the first three members of a series of allowed electrocyclic transformations: 1, butadiene to cyclobutene; 2, hexatriene to cyclohexadiene; 3, octatetraene to cyclooctatriene.

values of the similarity indices for conrotatory and disrotatory reaction paths systematically differ in such a way that higher r, or in other words, the lower extent of electron reorganization, is observed just for reactions that are allowed by the Woodward–Hoffmann rules (Table I).

Such an alternative reproduction of the - Woodward–Hoffmann rules is not, however, the only one that can be extracted from the values of r. Another interesting application, confirming the above intuitive interpretation of r as a measure of the ease of the reaction, is related to the existence of the quantitative parallel between the values of r_{RP} and the magnitude of the experimental activation energies in the allowed process. The existence of this parallel can be best demonstrated graphically in Figure 1, correlating the similarity index r_{RP}, calculated by a simple HMO method, with the activation energies for the first three members of the series of electrocyclic reactions, for which the experimental E_a values were available.

In contrast to electrocyclic reactions for which the parallel between the Woodward–Hoffmann rules and the least motion principle is entirely straightforward, the more complex situation is for cycloaddition and sigmatropic reactions where the values of similarity indices for alternative reaction mechanisms are equal so that the discrimination between allowed and forbidden reaction paths becomes impossible. The origin of this insufficiency was analyzed in subsequent studies[26,27] in which we demonstrated that the primary cause lies in the restricted information content of the index r_{RP}. In

order to overcome this certain limitation, several solutions were proposed. The simplest solution is based on the use of the so-called second-order similarity index g_{RP}. This index, introduced in direct analogy with the first-order index r_{RP}, is generally defined by eq 8, where $\tilde{\rho}_R(1,2)$ and $\tilde{\rho}_P(1,2)$ are pair density matrices of the corresponding molecules R and P.

$$g_{RP} = \frac{\int \tilde{\rho}_R(1,2)\tilde{\rho}_P(1,2) \, d\tau_1 \, d\tau_2}{(\int \tilde{\rho}_R^2(1,2) \, d\tau_1 \, d\tau_2)^{1/2}(\int \tilde{\rho}_P^2(1,2) \, d\tau_1 \, d\tau_2)^{1/2}} \quad (8)$$

The philosophy of this generalization is based on the following simple idea. According to quantum mechanics, all the information about the structure of a molecule is contained in the wave function. On passing from the wave function to density matrices, i.e., on integration over the coordinates of a certain number of electrons, part of this information is lost. The degree of this loss depends of course on the degree of reduction, i.e., on the number of coordinates over which the integration is performed, and the highest degree of loss is for the first-order matrices. This suggests that, on using the second-order or pair density matrices, the information content of the corresponding similarity indices will increase. The most important difference resulting from the use of pair density matrices is that they include, even if only partially, the electron correlation so that the increased information content of the second-order indices g_{RP} can be apparently related just to these correlation contributions. The comparison of values of g_{RP} and r_{RP}, again calculated from simple HMO wave functions, is given in Table I.

The most interesting result of such a comparison is that the original insufficiency of the similarity index **r** in the case of cycloaddition reactions is indeed remedied by the index **g**. This suggests that the role of the electron correlation is apparently higher in cycloaddition and sigmatropic reactions than in the electrocyclic ones. In this connection, it is also interesting to mention the case of the Cope rearrangement for which the discrimination between the allowed and forbidden reaction mechanisms is impossible with either the r_{RP} or the g_{RP} index. This especially delicate reaction was analyzed in a separate study[27] in which we demonstrated that the correct discrimination is required, in this case, to introduce higher than pair correlations in the so-called third-order similarity index g_{RP}.

(3) GENERALIZED AND INTEGRAL SIMILARITY INDICES

The philosophy of introducing the generalized and integral similarity indices arises from a simple idea to not only base the description of the reaction on two, however important, structures of the R and P but to also exploit for this purpose the information about all transient structures which may participate in a given reaction. The information about the structure of these species comes from the so-called overlap determinant method,[28] which is a recently introduced procedure for the characterization of the structural reorganization during the chemical reaction. The method is based on a simple intuitive idea that a chemical reaction is nothing but a specific transformation mutually converting the reactant into the product. Describing now the structure of these crucial molecular species by approximate wave functions, rather than relating the AO bases of the reactant and the product via the transformation matrix T after the topological transformation, the above abstract picture of a chemical reaction can be mathematically described by a mapping $F(q)$, converting, in

dependence on the continuous change of the parameter q, the wave function of the reactant into the wave function of the product. In our previous study,[28] we used for this purpose a simple trigonometric formula (eq 9), where the role of the generalized reaction coordinate is played by the variable φ changing within the range $(0,\pi/2)$.

$$\Phi(\varphi) = (1/N(\varphi))(\cos \varphi \Phi_R + \sin \varphi \Phi_P) \quad (9)$$

On the basis of the generalized wave function (eq 9), it is then possible to introduce the closely related topological density matrix $\Omega(\varphi)$, which is the basic quantity allowing the specification of the structure of transient species participating on the transformation of the system during its movement along the reaction path:

$$\Omega(\varphi) = N \int \Phi^2(\varphi) \, d\xi_1 \, dx_2 \, dx_3 \dots dx_N \quad (10)$$

For the purpose of similarity approach, this density matrix is used in the form of the so-called *generalized* similarity index $r_{RX}(\varphi)$;[29] the values of which provide, as can be seen from the definition equation (eq 11), the quantitative measure of the resemblance of an arbitrary transient species $X(\varphi)$ to the original reactant. This allows us to characterize the reaction

$$r_{RX}(\varphi) = \frac{Tr\Omega_R\Omega(\varphi)}{(Tr\Omega_R^2)^{1/2}(Tr\Omega^2(\varphi))^{1/2}} \quad (11)$$

not by one, even certainly important, value r_{RP} but by the whole dependence $r(\varphi)$ vs φ. The individual reactions, as well as the alternative reaction mechanisms, are then distinguished by the detailed form of these dependencies. Such a simple visual comparison of the individual dependencies is not, however, sufficiently precise. For the purpose of the quantitative discussions, it is, therefore, more convenient to give the above visual procedure a more precise quantitative form. The natural quantity for this purpose is the integral (eq 12), characterizing the extent of electron reorganization by the deviations between the actual dependence $r(\varphi)$ vs φ and the "standard" line $r(\varphi) = 1$, corresponding to the idealized hypothetical process during which the electron configuration is kept constant so that there is no electron reorganization at all.

$$J = \frac{\int_0^{\pi/2}(1 - r(\varphi)) \, d\varphi}{\int_0^{\pi/2} d\varphi} = 1 - 2/\pi \int_0^{\pi/2} r(\varphi) \, d\varphi \quad (12)$$

The results, the so-called *integral* similarity index,[29] vary again between 0 and 1, and its values are related to the extent of electron reorganization in such a way that low values of J correspond to minimal electron reorganization and vice versa. The practical use of the integral similarity index is entirely analogous as in the case of the "normal" index r_{RP} and originates from parallels with the least motion principle. We can thus expect that low values of J indicate an easy course of the reaction. The correctness of this simple intuitive criterion was confirmed in a number of examples covering the whole range of pericyclic reactions. Several such examples are given in Table II, from which it is evident that the concordance with the prediction of the Woodward–Hoffmann rules is in this case complete.

One of the most important features of the proposed approach is its complete independence of molecular symmetry. This opens the possibility of using this index as a new means of the systematic study of all the questions related to the problem of substituent effect in pericyclic reactivity. In this connection

Table II. Calculated Values of Integral Similarity Index J for Several Selected Pericyclic Reactions

reaction	mechanism	classification	J
butadiene/cyclobutene	conrotation	allowed	0.096
	disrotation	forbidden	0.195
hexatriene/cyclohexadiene	disrotation	allowed	0.085
	konrotace	forbidden	0.131
ethene dimerization	s + a	allowed	0.185
	s + s	forbidden	0.195
Diels–Alder reaction	s + s	allowed	0.160
	s + a	forbidden	0.165
Cope rearrangement	s + s	allowed	0.192
	s + a	forbidden	0.196
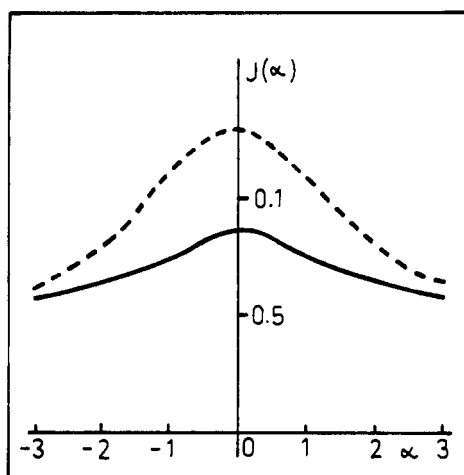
Figure 2. Calculated dependence of integral similarity index $J(\alpha)$ for the cyclization of 1-substituted butadiene to corresponding cyclobutanes on the magnitude of "substituent power" α. (Solid line corresponds to allowed conrotatory reaction; broken line corresponds to forbidden disrotatory reaction.)

it is, of course, necessary to say that some aspects of this problem (e.g., the regioselectivity) can be solved also by other existing techniques,[30-32] but various problems concerned with the possibility of substituent-induced violation of the Woodward–Hoffmann rules still lie beyond the scope of present methods. The possibility of the systematic study of all these questions by one universal similarity approach is therefore interesting and useful.

(4) SUBSTITUENT EFFECT ON VALIDITY OF WOODWARD–HOFFMANN RULES

Several typical examples demonstrating the practical use of the approach just for evaluating the possibility of eventual substituent-induced violation of the Woodward–Hoffmann rules are discussed in the studies.[33,34] The philosophy of these studies is very simple and consists of the analysis of general trends manifesting themselves in the dependence of the similarity index J on the quantities characterizing the substitution. Within the framework of the simplest HMO model where the substitution is modeled by the values of the Coulombic integral α, the above philosophy leads to the determination and the analysis of the dependencies $J(\alpha)$ vs α. A typical example of such a dependence is given in Figure 2, describing the electrocyclic transformation of 1-substituted butadienes to corresponding cyclobutenes. The interpretation of these dependencies is thoroughly discussed in the study[33] where it is also possible to find all the mechanistic implications which can be deduced from the corresponding curves. Here we, therefore, confine ourselves only to the brief recapitulation of the most important results.

Thus, for example, taking into account that according to the least motion principle the low values of J generally imply

an easy course of reaction, the decrease of corresponding $J(\alpha)$ vs α curves with increasing $|\alpha|$ can be regarded as indicating the facilitation of the process for both conrotatory and disrotatory cyclization. This facilitation as well as expected retardation in the case of conrotatory cyclization of 2-substituted cyclobutenes[33] is indeed experimentally confirmed.[35,36]

Another important nontrivial conclusion which can be deduced from the above dependencies is concerned with the problem of eventual substituent-induced violation of the Woodward–Hoffmann rules. The decisive role in this respect is played by the different sensitivity of corresponding conrotatory and disrotatory curves with respect to the variation in α. As can be seen from Figure 2, these curves approach one another, but this approach has only asymptotic character so that, even for high values of α, the curves display no tendency to cross. This suggests that the inequality $J_{dis} > J_{con}$, ensuring the preference of concerted conrotation, is valid not only for the parent nonsubstituted case but also for the whole range of α. This result is very interesting since it numerically confirms the well-known empirical fact that the Woodward–Hoffmann rules are usually a little sensitive to the substitution so that terms such as "allowedness" and "forbiddeness" retain their meaning irrespective of eventual deviations from the perfect symmetry.

In connection with this conclusion, it is of course necessary to be aware of the fact that its validity is proved, by the above approach, only in a given concrete case. This, however, represents no important problem since the formalism itself is completely general so that in applying it to any other case the possibility of eventual exceptions could be disclosed. As an interesting example where such a substituent-induced violation of the Woodward–Hoffmann rules could take place, the isomerization of substituted butadienes to corresponding [1,1,0]bicyclobutanes can be mentioned.[33] In this connection, it would be certainly interesting to confront our theoretical prediction with the experiment, but the lack of convenient experimental data makes such a confrontation unfeasible so far.

(5) SIMILARITY INDEX AND LEAST MOTION PRINCIPLE

The broad practical use of the similarity approach is based on the interpretation of the similarity index in terms of the least motion principle. Since in all previous examples this interpretation has remained only on the level of an intuitively expected parallel, it would certainly be useful to support the existence of such a parallel more precisely.[37]

The simplest situation is the case of the index r_{RP} whose relation to the extent of electron reorganization can be simply demonstrated on the basis of the transformation of the density matrices Ω_R and Ω_P from the original basis of AO into the common basis of molecular orbitals of one of the reaction partners. Let it be, for example, the basis of the MO of the reactant. In this basis the matrix Ω_R has the especially simple diagonal form (eq 13), due to which the general expression for the similarity index r_{RP} can be substantially simplified.

$$(\Omega_R)^{MO(R)} = C^{-1}\Omega_R^{AO}C \qquad (13a)$$

$$(\Omega_R)^{MO(R)} = \text{diag}(2, 2, ... 2, 0, 0 ... 0) \qquad (13b)$$

If we compare the resulting form of the matrices Ω_R and Ω_P (eq 14) on the basis of the reactant's MO, it is possible to see that the original definition relation (eq 7b) can be rewritten in the form of eq 15, from which the physical meaning of r_{RP}

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$$(\Omega_p)^{MO(R)} = \begin{pmatrix} \eta_{11}\eta_{12}....\eta_{1n} \\ .... \\ \eta_{n1}\eta_{n2}....\nu_{nn} \end{pmatrix} \quad (14)$$

$$r_{RP} = \sum_{i}^{occ} \eta_{ii}/N \quad (15)$$

is evident. Thus, e.g., taking into account that the matrix elements η_{ii} correspond to that part of the electron density of the product which is formally accumulated in the occupied molecular orbitals of the reactant, the value of the similarity index given by the ratio (eq 15) just gives the part of the total number of N electrons which remains "unexcited" in the subspace of occupied molecular orbitals of the reactant. The extent of the excitation can then be naturally characterized by the quantity ξ (eq 16), whose relation to the similarity index is evident.

$$\xi = (N - \sum^{occ} \eta_{ii})/N = 1 - r_{RP} \quad (16)$$

In connection with this simple relation, it is interesting that an analogous expression holds also in the case of a more detailed description in terms of the integral index J. This relation is clearly visible if we realize that the expression on the right side of eq 12 is nothing but the relation for the mean value of the generalized similarity index $r(\varphi)$. Using this identity, the original eq 12 can be alternatively rewritten in the form of eq 17, from which the difference between the characterization of electron reorganization in terms of r and J becomes evident.

$$J = 1 - \bar{r}_{RP} \quad (17)$$

(6) SIMILARITY CRITERION FOR DISCRIMINATING BETWEEN ONE-STEP AND STEPWISE REACTION MECHANISMS IN PERICYCLIC REACTIONS

In all the previous applications we have so far dealt with, the similarity approach was applied only to the so-called concerted reactions, the typical feature of which is that they proceed as a simple process in one elementary step. Such a picture of the chemical reaction need not be, however, always realistic since complex reaction mechanisms involving two or more reaction steps can be in some cases more advantageous. With this in mind, we have attempted to generalize the original similarity approach so as to be applicable to these more complex reaction schemes as well. Of primary interest in this connection was the generalization of the approach, allowing it to be applied for the evaluation of relative ease of the alternative reaction paths.[38] Such a generalization is again based on the parallel with the least motion principle, in terms of which the relative ease of concerted and stepwise reaction paths is estimated on the basis of comparison of appropriate quantities characterizing the extent of electron reorganization in idealized one-step and stepwise reaction schemes. Since in the case of purely concerted reaction paths the relation of the similarity index r_{RP} to the extent of electron reorganization was discussed previously, it is necessary to mention only the case of stepwise reaction paths which in the case of pericyclic reactions are extremely simple and involve only one intermediate. The problem of the appropriate generalization of the similarity approach was discussed in detail in our recent study[38] in which we demonstrated that the overall extent of reorganization in

the whole two-step process (eq 18) can be expressed in terms

$$R \rightarrow I \rightarrow P \quad (18)$$

of similarity indices of individual reaction steps by the relation

$$\xi_{stepwise} = (1 - r_{RI}) + r_{RI}(1 - r_{IP}) = (1 - r_{RI}r_{IP}) \quad (19)$$

Since the extent of reorganization in the one-step concerted process is given by eq 16, it is possible to expect that the relative ease of concerted and stepwise reaction mechanisms can be estimated on the basis of comparison of the similarity index r_{RP} with the product $r_{RI}r_{IP}$. If the value of r_{RP} is higher than the value of the product, the concerted reaction mechanism can be expected to be preferred. On the other hand where the product is higher, a preference for two-step reaction mechanisms can be expected. As an example of the practical use of the above criterion, the electrocyclic transformation of butadiene to cyclobutene will be discussed. Since the detailed procedure of determination of similarity indices for both alternative reaction paths is sufficiently described in the original study, it is not necessary to go into the details and the resulting final values can be directly given eq 20:

$$r_{RP}^{con} = 0.724 \qquad r_{RI}^{con} = r_{RI}^{dis} = 0.851$$

$$r_{RP}^{dis} = 0.500 \qquad r_{IP}^{con} = r_{IP}^{dis} = 0.781 \quad (20)$$

For the sake of completeness, we note only that the values of similarity indices are again derived from a simple HMO model. From these values, several interesting conclusions can be deduced immediately. First, the comparison of relative ease of conrotatory and disrotatory reaction paths for concerted reaction mechanism is deduced. As can be seen from the corresponding indices r_{RP}, the conrotatory cyclization preferred by the Woodward–Hoffmann rules is clearly favored by the least motion criterion as well.

A little bit more complex situation is the case of nonconcerted reaction paths where the values of corresponding indices for both conrotatory and disrotatory reaction paths are the same. At first sight a surprising result this is, however, entirely reasonable since the equivalence of both alternative stepwise reaction paths fits with the well-known lack of stereospecificity of these paths. Much more interesting than this trivial result is the evaluation of the relative ease of concerted and stepwise reaction paths. Thus, for example, it is possible to see that the direct cyclization should be preferred over the stepwise path for allowed reaction ($r_{RP} > r_{RI}r_{IP}$) while in the case of forbidden disrotation the preferred reaction path is the stepwise one. This result is very interesting not only for being in harmony with what was intuitively expected from the Woodward–Hoffmann rules but also for corresponding remarkably with what is predicted for the mechanism of the reaction from available theoretical data.[39-41] Especially interesting in this connection is the case of forbidden disrotatory reaction, for which both semiempirical and ab initio calculations predict the reaction path to be asynchronous. The limiting case of this asynchronous reaction path is then our idealized two-step mechanism via biradical intermediate.

(7) SIMILARITY INDICES AND EVANS–DEWAR CONCEPT OF AROMATICITY OF TRANSITION STATES

As a last example demonstrating the broad possibilities of the similarity approach in the theory of pericyclic reactions, the problem of the theoretical justification of the Evans–Dewar concept of aromaticity of transition states will be mentioned. The basis of this concept is a simple intuitive parallel between

Table III. Calculated Values of Similarity Index $r_{\neq,ref}$ for Several Selected Pericyclic Reactions

reaction	mechanism[a]	$r_{\neq,ref}$	
		arom ref	antiarom ref
butadiene/cyclobutene	conrotation	0.851	0.982
	disrotation	0.986	0.737
hexatriene/cyclohexadiene	disrotation	0.896	0.973
	conrotation	0.992	0.807
ethene dimerization	s + a	0.781	1.000
	s + s	0.997	0.809
Diels–Alder reaction	s + s	0.842	0.988
	s + a	0.980	0.855
Cope rearrangement	s + s	0.834	0.998
	s + a	0.976	0.872

[a] Upper value corresponds to the allowed and the lower value corresponds to the forbidden reaction mechanism.

the ease of certain reactions and the arrangement of corresponding transition states. Thus, for example, the ease of Diels–Alder reactions is related to the fact that transient structures created on approaching the diene and dienophilic components are isoconjugated or, in another words, topologically equivalent with aromatic benzene and as such should, therefore, be stabilized energetically. More recently this intuitive parallel was generalized by Dewar,[42] who included it into the broader context of selection rules in chemical reactivity. Within the framework of this incorporation, the condition of the discrimination between the allowed and the forbidden reactions is expressed by a simple rule that (thermally) allowed pericyclic reactions proceed via aromatic transition states.

The proposed theoretical justification of this empirical criterion arises from the simple idea of using the similarity index (eq 21) as a quantitative measure of the expected

$$r_{\neq,ref} = (1/N_{\neq,ref})Tr\Omega^{\neq}\Omega_{ref} \qquad (21)$$

resemblance of the transition states of allowed pericyclic reactions with ideal aromatic standards. This of course requires the knowledge of the density matrices of both the transition states and reference standards. The problem of the choice of these structures is discussed in detail in the original study[43] so that the necessary arguments can be found there. Here we confine ourselves to a brief recapitulation of the resulting conclusions. The situation is relatively simple with the matrix Ω_{ref} since the corresponding standards can be naturally identified with ideally aromatic structures such as benzene in 6-electron transformations and Möbius cyclobutadiene in 4-electron transformations. In the question of the matrix $\Omega^{\neq}$, an important simplification comes from the topological description in terms of generalized overlap determinant method. It appears that the number of properties intuitively connected with the transition states can be found with critical structures $X(\pi/4)$.[28,43] On the basis of this parallel, the density matrix $\Omega^{\neq}$ is approximated by the density matrix $\Omega(\pi/4)$ of the critical structure. The original equation (eq 21) can thus be rewritten in the form of eq 22, used for

$$r_{\neq,ref} = (1/N_{\neq,ref})Tr\Omega_{ref}(\pi/r) \qquad (22)$$

the practical calculation of corresponding indices. The calculated values of these indices are summarized in Table III where the values are included for comparison and also for indices derived from the use of antiaromatic standards as the natural counterparts to ideally aromatic reference structures. As can be seen from Table III, the values of similarity index

do confirm the Evans–Dewar classification completely, since in allowed reactions the similarity to aromatic standards is always dominating.

(8) CONCLUSIONS

Previously, a number of examples were presented that demonstrates the broad possibilities brought to the theory of pericyclic reactions by models quantitatively exploiting the idea of molecular similarity. In spite of a considerably broad scope of all these applications, the possibilities of the approach are still not exhausted, and its formalism is still capable of further methodological development.

One of the most interesting such applications is concerned with the extension of the *generalized* similarity indices beyond the scope of purely concerted reactions to processes involving the participation of intermediates. Such a generalized model of chemical reaction could be then used for the theoretical analysis of mechanisms of pericyclic reactions in terms of the least motion principle or from the point of view of concertedness.[44]

Another broad area of the exploitation of similarity approach is concerned with the problem of higher order similarity indices which, owing to partial inclusion of electron correlation, could be used as a new specific means of the study of correlation effects in pericyclic reactions.

Although some of these problems were already discussed in our studies,[45,46] the vast majority of the above questions are completely open and still wait for their systematic exploitation.

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