TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY. EVANS–DEWAR PRINCIPLE IN TERMS OF MOLECULAR SIMILARITY APPROACH

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The Evans–Dewar concept of aromaticity of transition states is given new theoretical support in terms of the similarity approach to chemical reactivity. The principal goal of this approach consists in providing a simple, chemically lucid justification for the legitimacy of the original intuitively formulated concept.

INTRODUCTION

A primary question accompanying the advent of the Woodward–Hoffmann rules concerns the elucidation *of the factors responsible for their remarkable universality.* This concerns above all the considerable insensitivity to deviations from perfect symmetry. This suggests that the molecular symmetry on which the original formulation was based is not probably the true decisive factor. The problem of the theoretical foundations underlying the universality of Woodward–Hoffmann rules has therefore become the subject of numerous theoretical studies.[1–6] They resulted in the nowadays generally accepted opinion emphasizing the importance of molecular topology rather than molecular symmetry. The characteristic whose conservation is required for selection rules to hold is therefore not the symmetry of molecular orbitals, but their nodal structure. For the analysis of this nodal structure, various techniques have been designed, differing in the degree of universality and mathematical complexity.[1–3,7,8] Of these, one of the simplest arises from the parallel intuitively felt by Evans and Warhurst[9] between the ease of certain reactions and the arrangement of corresponding transition states. For example, the ease of most Diels–Alder reactions is related to the fact that the transient structure created on approaching the diene and dienophilic components is isoconjugate (in another words topologically equivalent) with aromatic benzene and that it should therefore exhibit, at least in part, similar aromatic stabilization to benzene itself. This simple idea was revived by Dewar,[5] who included it in his concept of aromaticity of transition states. This concept is expressed by a simple rule that

(thermally) allowed pericyclic reactions proceed via aromatic transition states. Our aim in this paper is to demonstrate that this empirically found powerful concept, theoretically supported some time ago by Aihara,[10] can also be given another independent justification in terms of the recently proposed molecular similarity approach.[11]

The basic idea of this approach is very simple and consists in the direct numerical evaluation of the resemblance of the electron structure of expected transition states with the appropriate aromatic and/or antiaromatic standards. For the qualitative characterization of this resemblance, the so-called similarity index is used, the values of which do confirm that the transition states in allowed reactions are indeed remarkably similar just to aromatic reference standards (benzene and Möbius cyclobutadiene in six- and four-electron transformations, respectively), whereas for forbidden reactions the high resemblance to antiaromatic standards is analogously observed.

In connection with this result it is necessary, however, to remark that the idea of the numerical characterization of molecular similarity by the values of the similarity index is, of course, only empirical and its *legitimacy is supported by the agreement with observed* data rather than by some theoretical arguments. In spite of the empirical nature of the approach, we nevertheless believe that the new light it throws on the old problem of aromaticity and antiaromaticity of pericyclic reactions is interesting and that its future systematic use may contribute to the better understanding of the factors responsible for the remarkable differences in the nature of electron reorganization in allowed and forbidden reactions.

THEORETICAL

The basic idea of the proposed approach arises from the recently formulated method of the so-called overlap determinant[7] and its subsequent generalizations to the characterization of similarity of molecular structures.[11] The quantity characterizing the 'similarity' of two isoelectronic molecules A and B is the so-called similarity index, $r_{A,B}$, defined in terms of topological density matrices, Ω_A and Ω_B,[11] by

$$r_{A,B} = \frac{Tr\,\Omega_A \Omega_B}{\mathcal{N}_{A,B}} \quad (1)$$

Owing to normalization by the factor $\mathcal{N}_{A,B}$, the values of this index vary between 0 and 1. The limiting value 1 can be obtained only in the case of two identical structures and the extend of deviations from unity just measures the similarity of the corresponding structures. The normalization factor ensuring the above properties of the similarity index is generally defined by

$$\mathcal{N}_{A,B} = (Tr\,\Omega_A^2)^{1/2}(Tr\,\Omega_B^2)^{1/2} \quad (2)$$

If the density matrices are derived from the one-determinantal wavefunctions and thus obey the idempotency relations

$$Tr\,\Omega_A^2 = Tr\,\Omega_B^2 = 2N \quad (3)$$

then the following equation results:

$$\mathcal{N}_{A,B} = 2N \quad (4)$$

which appears in the original definition of the similarity index[11] (N is the number of electrons in the system). The index defined by equation (1) represents a very flexible universal tool for the characterization of the electronic structure of the molecules, and some possibilities for its use were discussed in previous papers.[11-13] In this paper, we want to demonstrate another interesting application of the similarity index for the purpose of quantitative confirmation of the Evans–Dewar concept of the aromaticity of transition states in pericylic reactions. Such an exploitation is based on the simple idea of using the similarity index as a quantitative measure of the resemblance of electron structures of expected transition states with the appropriate aromatic (for allowed reactions) or antiaromatic (for forbidden ones) reference structures. The corresponding similarity index $r_{\neq,\text{ref}}$ is then defined by

$$r_{\neq,\text{ref}} = \frac{Tr\,\Omega_{\neq}\Omega_{\text{ref}}}{\mathcal{N}_{\neq,\text{ref}}} \quad (5)$$

where $\Omega_{\neq}$ and Ω_{ref} represent the density matrices for the expected transition state and the appropriate reference structure, respectively.

The practical use of this simple philosophy depends, of course, on how reliably the corresponding density matrices $\Omega_{\neq}$ and Ω_{ref} are known. The situation is relatively simple with reference structures where

Dewar's classification suggests benzene as the natural model for six-electron and Möbius cyclobutadiene for four-electron allowed transformations. Similarly, in the case of forbidden reactions the same standards can be expected to be Möbius benzene and cyclobutadiene. More complex and for the reliability of the approach also more important is therefore the question of the knowledge of the density matrices $\Omega_{\neq}$ for the transition states.

Before starting the discussion of the appropriate choice of this density matrix, we consider it useful to mention briefly also some linguistic problems connected with the use of the term 'transition state' within the framework of the Evans–Dewar scheme. The problem is that the term transition state is reserved for the saddle points on potential energy hypersurfaces, whereas the Evans–Dewar scheme operates with the concept of aromaticity without any reference to potential hypersurfaces. Even if this circumstance is not perhaps too important for a majority of concerted reactions which are believed to proceed concertedly via true saddle points, there are nevertheless a number of exceptions. The possibility of such exceptions was indeed challenged by Dewar, who proposed a simple rule according to which the multi-bond reactions cannot be synchronous[14] and should proceed in several steps or stages. In order to include also these more complex situations and hence to avoid the above semantic complications, we consider it convenient to modify the original formulation, without altering its impact in any way, by substituting the precise term transition state by the looser term 'critical structure.' The final formulation could then be e.g., that (thermally) allowed reactions proceed via aromatic and forbidden via antiaromatic critical structures.

Let us proceed now to the discussion of the fundamental question of the structure of critical species (alias transition states) required for the formalism expressed by equation (5). An interesting solution to this fundamental problem is provided by the recently proposed topological approach based on the so-called overlap determinant method. Since this method has been thoroughly described previously,[15] we consider it sufficient to present only the basic principles to the extent necessary for the purpose of this study. In the framework of this method the chemical reactions is generally regarded as an abstract continuous mapping* transforming the reactant into the product.

Describing now the structure of these key molecular species by the approximate wave functions ψ_R and ψ_P, then after the necessary transformation of the molecular orbitals of the product into the common basis of atomic orbitals, described within the framework of the

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* A more precise discussion concerning the mathematical background of the formalism is given in the Appendix.

overlap determinant method by the so-called assigning tables, the corresponding mapping can be mathematically described by a transformation converting the wavefunction of the reactant into the wavefunction of the product. Since the construction of the assigning tables has been sufficiently described previously,[7] we do not repeat it here. We recall, however, that the form of these tables depends on the actual reaction mechanism of the transformation so that by appropriate choice of these tables the allowed and forbidden reactions can be analysed separately.

Assuming that the form of the assigning tables is known, it is possible to continue with the more detailed specification of the mapping depicting the structural tranformation of the reactant into the product. To describe this transformation a simple trigonometric formula [equation (6)] was proposed,[15]

$$\psi(\varphi) = \frac{1}{\mathcal{N}(\varphi)} \, (\psi_R \cos \varphi + \psi_P \sin \varphi) \qquad (6)$$

characterizing the corresponding structural change by the continuous variation of the argument φ within the interval $\langle 0, \pi/2 \rangle$. Having introduced the generalized wavefunction (6), it is only a matter of straightforward generalization to introduce the so-called topological density matrix $\Omega(\varphi)$ by

$$\Omega(\varphi) = N \int \psi^2(\varphi) \, d\xi_1 \ldots d\xi_N \, dr_2 \ldots dr_N \qquad (7)$$

which is the basic quantity describing in the overlap determinant method the structure of transient species through which the system passes during its movement along the reaction path.

To analyse the structure of these species, a simple method based on the diagonalization of corresponding topological density matrices for different values of the argument φ was proposed.[15] This analysis revealed the remarkable differences in the character of electron reorganization of allowed and forbidden reactions and, at the same time, revealed the crucial role of the critical structure $X(\pi/4)$ described by the matrix $\Omega(\pi/4)$, the properties of which are to a considerable extent analogous to those of transition states. For the purpose of this study, the parallel between the critical structures $X(\pi/4)$ and the transition states can be the most simply demonstrated on the values of similarity indices $r_{R,X(\varphi)}$ and $r_{P,X(\varphi)}$, defined by

$$r_{R,X(\varphi)} = \frac{Tr \, \Omega(0)\Omega(\varphi)}{\mathcal{N}_{R,X(\varphi)}} \qquad (8a)$$

$$r_{P,X(\varphi)} = \frac{Tr \, \Omega(\pi/2)\Omega(\varphi)}{\mathcal{N}_{P,X(\varphi)}} \qquad (8b)$$

characterizing the resemblance of the general transient species to the reactant and the product, respectively. For these indices the following relationships Hold:

$$r_{R,X(\pi/4)} = r_{P,X(\pi/4)} \qquad (9a)$$

$$r_{R,X(\varphi)} > r_{P,X(\varphi)} \quad \text{for } \varphi < \pi/4 \qquad (9b)$$

$$r_{R,X(\varphi)} < r_{P,X(\varphi)} \quad \text{for } \varphi > \pi/4 \qquad (9c)$$

These equations imply that the structure $X(\pi/4)$ described by the matrix $\Omega(\pi/4)$ bisects the reaction path into two regions, $\varphi < \pi/4$ and $\varphi > \pi/4$, in such a way that all the structures in the first region are more similar to the reactant than to the product, whereas for the second region the similarity is reversed. The critical point $X(\pi/4)$ itself is then characterized by the property that its similarity to both the reactant and the product is the same, so that it lies just at the borderline of both regions. In view of the properties expressed by equation (9), we propose to call these regions the region of the reactant and the product. In this connection it is of interest that the analogous possibility of dividing into the so-called catchment regions was proposed by Mezey[16] for potential energy hypersurfaces. The above intuitive analogy suggesting the possibility of a certain parallelism between our critical structures $X(\pi/4)$ and the critical points on the energy hypersurface (without explicitly specifying the type of the critical point) then opens the way to the practical exploitation of equation (5). Such an exploitation is based on replacing the transition-state density matrix $\Omega_{\neq}$ by the density matrix $\Omega(\pi/4)$ of the critical species. The original equation thus transforms to the form

$$r_{\neq,\text{ref}} = \frac{Tr \, \Omega(\pi/4)\Omega_{\text{ref}}}{\mathcal{N}_{X(\pi/4),\text{ref}}} \qquad (10)$$

The values of the similarity index calculated using this equation for several types of pericyclic reactions are summarized in Table 1. In order to maintain the con-

Table 1. Calculated values of similarity indices for selected pericyclic reactions

Reaction	Mechanism[a]	$r_{\neq,\text{ref}}$	
		Aromatic ref.	Antiaromatic ref.
Ethene + ethene	$s + s$	0·781	1·000
$\rightarrow$ cyclobutane	$s + a$	0·997	0·809
Butadiene $\rightarrow$	Disrotatory	0·851	0·982
cyclobutene	Conrotatory	0·986	0·737
Diels–Alder	$s + a$	0·842	0·988
reaction	$s + s$	0·980	0·855
Hexatriene $\rightarrow$	Conrotatory	0·896	0·973
cyclohexadiene	Disrotatory	0·992	0·807
Cope	$s + a$	0·834	0·998
rearrangement	$s + s$	0·976	0·872
Butadiene $\rightarrow$	$s + s$	0·863	0·791
bicyclobutane	$s + a$	0·830	0·803

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

tinuity with our previous studies dealing with the applications of the similarity approach,[7,12] the same series of reactions will be analysed. This allows us to reduce the amount of necessary technical detail, which can be found in the previous studies. Hence we shall give here only the most basic piece of information, viz. that the wavefunctions describing the reactant and the product were obtained by simple HMO method compatible with the topological nature of the approach.

RESULTS AND DISCUSSION

Let us attempt now to discuss some general conclusions arising from Table 1. The most important result is that the predictions of the Evans–Dewar classification are indeed confirmed in most cases. In harmony with this classification, the values of the similarity indices confirm that the critical structures approximating the transition states for allowed reactions are remarkably similar to the aromatic reference structures, whereas for forbidden reactions the similarity to antiaromatic standards dominates. This general tendency can be most clearly demonstrated, .e.g, on the values of $r_{\neq,\text{ref}}$ for the electrocyclic transformation of the butadiene and hexatriene to clyclobutene and cyclohexadiene, respectively, where the similarity of the critical structure $X(\pi/4)$ to the aromatic standards (Möbius cyclobutadiene and benzene) is very high (0·986 and 0·992, respectively) in comparison with the considerably lower similarity to 'wrong' antiaromatic structures (0·737 and 0·807, respectively). On the other hand, in the case of forbidden reactions the situation is reversed and the dominant similarity is encountered with antiaromatic standards (compare, e.g., the values of 0·982 vs 0·851 for butadiene and 0·972 vs 0·896 for hexatriene cyclization).

An interesting example of the extremely high similarity to antiaromatic reference structure is observed in the case of $2s + 2s$ ethene dimerization, where the resemblance of the critical structure to the antiaromatic cyclobutadiene is so high that they even become completely identical ($r_{\neq,\text{ref}} = 1\cdot000$). At the same time, the similarity to the corresponding aromatic standard (Möbius cyclobutadiene) for the allowed reaction is not so ideal, even though it is still very high ($r_{\neq,\text{ref}} = 0\cdot997$). The origin of this remarkable high similarity to antiaromatic standards in forbidden reactions is not clear to us. Nevertheless, it is interesting that the same behaviour is observed also in the Diels–Alder reaction and Cope rearrangement, which belong to the broader class of multi-bond reactions, the specific position of which was stressed by Dewar.[14] This certain specificity, manifesting itself in our case by the remarkable antiaromaticity of critical structures in forbidden reactions, has, however, no impact on the validity of the Evans–Dewar classification, since, as can be seen from Table 1, the corresponding values (0·997 vs 0·809 for $s + a$ ethene dimerization, 0·976 vs 0·872 for $s + s$ Cope rearrangement and 0·980 vs 0·855 for the Diels–Alder reaction) clearly confirm that the critical structures are still considerably aromatic.

The only case for which the disagreement with the Evans–Dewar classification is encountered is thus the cyclization of butadiene to bicyclobutane, where the aromatic reference structure (Möbius cyclobutadiene) is surprisingly a more convenient model of the transition state than the antiaromatic one even for the forbidden $s + s$ cyclization (0·863 vs 0·791). This result is surprising but since this reaction is also puzzling for other techniques (thus, e.g., the usual correlation diagrams fail to determine the preferred reaction mechanism correctly[17]), we believe that the above result need not indicate the failure of the similarity approach. Rather, it is possible that the electron reorganization is in this case so atypical that it probably exceeds the scope of applicability of the Evans–Dewar classification. Useful conclusions which, to a certain extent, confirm the legitimacy of the above considerations can be obtained also by comparing the absolute values of individual similarity indices. If we compare from this point of view the similarity of allowed critical structures with corresponding aromatic standards, it is possible to see that whereas in all cases of 'normal' pericyclic reactions the corresponding indices are very close to unity, in the conflicting case of butadiene to bicyclobutane rearrangement they are much lower. This suggests that the aromatic structure (Möbius cyclobutadiene) which provides a perfect model of the critical structure in 'normal' cases ceases to be a good model here so that another, so far unknown, model should approximate the critical structure even better. In this connection the question of whether the anomalous character of the critical structure has or can have some specific implications for the mechanism of this reaction, e.g. in indicating the possibility of a multi-step course, thus arises.[18] The decisive role in this respect belongs especially to whether the confirmed aromaticity of critical structures in allowed reactions automatically ensures that these structures correspond to true transition states (saddle points) ensuring the concerted nature of the process, or whether the stepwise reaction mechanisms is also possible. Analogous, even if reversed, problems arise then also in the case of forbidden reactions where the question is whether the non-concerted stepwise mechanism can be anticipated from the fact that the antiaromatic critical structures usually display Jahn–Teller instability.

Even if a number of examples provided by sophisticated quantum chemical calculations seem to support this hypothesis,[18-20] apparent exceptions preventing any final decision also exist.[14] In spite of these uncertainties, we believe that the possibility of the quantitative theoretical support of the Evans–Dewar

classification is important enough to warrant further study of the similarity approach.

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APPENDIX

The fundamental concept on which the whole formalism of the generalized overlap determinant method is based is the concept of the *space of structures*, which is defined as a subspace of the Hilbert space of the electron wavefunctions. This generally m-dimensional subspace is spanned by the eigenfunctions of the Hamiltonian of the system:

$$\psi = \sum_{i=1}^{m} c_i \psi_i \qquad (A1)$$

The dimension of this space, i.e. the number of linearly independent basis functions, is in every particular case determined by the desired accuracy of description. The simplest case corresponds in this respect to the situation where only the crudest description of the reaction as a transformation of the reactant to the product without taking into account the eventual inclusion of possible intermediates is sufficient. In this case the space of structures is two-dimensional and its basis is formed by the electron wavefunctions ψ_R and ψ_P. Equation (A1) then reduces to the form

$$\psi = c_R \psi_R + c_P \psi_P \qquad (A2)$$

This equation implies that in order to model the reaction as a continuous transformation of the reactant into the product, a coupling of the coefficients c_R and c_P is required. This coupling, generally characterized by a change of one variable representing the generalized reaction coordinate, can be realized by an arbitrary continuous and monotonous function as, e.g., the proposed trigonometric formula. This simplest two-dimensional space of structures can, of course, be generalized further by including as the basis functions the wavefunctions of any additional species, e.g. of an intermediate, reflecting the more detailed mechanistic picture of the system.

The critical structure X is defined in the simplest case of two-dimensional space of structures as a species characterized by the same 'similarity' with respect to the reactant and to the product. This requirement, mathematically expressed by

$$r_{RX} = r_{PX} \qquad (A3)$$

is identically fulfilled for c_R, c_P satisfying the equation

$$c_R = c_P \qquad (A4)$$

which in our case immediately leads to the universal value $\varphi = \pi/4$. Using relationships similar to equation (A4), the critical structures can be analogously defined also in the case of more than a two-dimensional space of structures. Some possibilities of the exploitation of such a generalized approach for the characterization of concertedness in pericyclic reactions can be found elsewhere.[21]