
**TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY.
VALENCY CHANGES IN THE COURSE OF CHEMICAL REACTIONS**

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The Jug and Gopinathan approach to the use of valency changes for the characterization of chemical reactions is generalized by incorporating it into the framework of the recently proposed topological description of chemical reactivity in terms of the overlap determinant method. The conclusions of the simple topological analysis agree with the results of the direct quantum chemical treatment, indicating thus that the overlap determinant method depicts correctly the principal features of the electron density reorganization occurring during the chemical reactions.

One of the fundamental concepts of organic chemistry is the concept of valency, on the basis of which an immense number of empirical findings accumulated by the classical structural theory could be classified and systemized. For a deeper justification of this theory, frequent attempts have been made over the past decade to incorporate the valency concept into the wider scope of the theoretically founded quantum chemical description of molecular structure. The first to attempt at such generalization were probably Armstrong and coworkers¹ who defined the valency within the CNDO approximation in terms of the so-called Wiberg index². Although this original definition was later extended to more sophisticated semiempirical and *ab initio* techniques in both orthogonal and nonorthogonal basis sets³⁻¹⁰, the basic idea of all such generalizations remains virtually unchanged. The most significant consequence arising from this quantum chemical generalization concerns the fact that the valency no longer needs to attain, as in the classical theory, only integer values. Nevertheless, the calculated valencies, at least in the case of usual molecules, approach the classical integer values rather closely. The advantage of the quantum chemical generalization thus appears above all for various special structures such as the hypervalent clusters CLi_6 , OLi_4 , OLi_6 , etc., where the classical description completely fails, whereas the new definition allows us to obtain a sufficiently illustrative picture of bonding. Similar complications can also occur for various nonclassical structures which may appear as intermediates or transition states in chemical reactions.

In view of the successful application of the valency concept to the description of hypervalent structures, Gopinathan and Jug¹¹⁻¹³ have recently proposed its use also to the characterization of the above nonclassical species. Stimulated by the interesting results of these studies we suggest in this paper a modification of the original approach by incorporating the valency concept into the framework of the recently formulated description of chemical reactivity in terms of the generalized overlap determinant method.

RESULTS AND DISCUSSION

Since the overlap determinant method as well as its generalizations have been described sufficiently in the literature^{14,15}, we will confine ourselves to a brief recapitulation of its basic principles to an extent necessary for the purpose of this study. The structures of the reactant and the product are characterized within the framework of the overlap determinant method by an approximate wave function (the so-called bonding function) constructed from the individual chemical bonds that in a given reaction constitute the irreducible core. As a consequence of this simplification disregarding all the bonds that do not take a direct part in the reaction, each of the involved atoms bears just one atomic orbital participating in the bonds of the irreducible core. This approximation implies that from the total valency of each atom, the overlap determinant method describes only a certain "topologically active" part attaining a maximum value of unity irrespective of the chemical nature of the corresponding element. A certain loss of chemical information resulting from the uniformity of the values of the topologically active valencies does not detract, however, from the applicability of the generalized method to the description of the valency changes during chemical reactions. As will be shown later, the variation in the topologically active valencies reproduces perfectly the variation in the total valencies. This confirms the basic assumptions of the topological approach according to which the electron reorganization involves particularly bonds of the irreducible core while the remaining bonds are left virtually unchanged. Such a simplified picture of chemical reaction also immediately suggests the possibility of renormalizing the above introduced topological valencies to the common "classical" scale by adding a certain correction corresponding to the bonds initially neglected in the construction of the irreducible core. Since, as has been stressed above, these bonds play no active part in the reaction, such an extension has only the meaning of an unimportant additive correction which has no effect on the "topologically active" valencies.

After having summarized the specific features accompanying the definition of the valency within the framework of the overlap determinant method, let us proceed to its extension to the description of chemical reactions. This extension is directly based on the recently suggested generalization of the overlap determinant method describing the chemical reaction as a continuous process in which the bonding function Φ_R of the reactant is converted *via* the stage of all transient species $X(\varphi)$ into the product bonding function Φ_P . To describe this transformation it is possible to use, in principle, any mapping satisfying the requirement of continuity and mutual uniqueness. In this study we employ, similarly as in the original paper¹⁵, a simple relation (1) selected on the basis of analogy with the trigonometric formula by Pancir¹⁶,

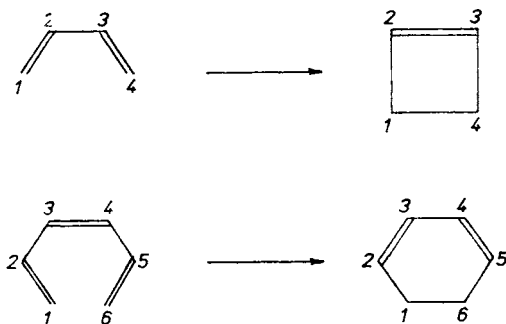
$$\Phi(\varphi) = \frac{1}{N(\varphi)} \{ \cos \varphi \Phi_R + \sin \varphi \Phi_P \}. \quad (1)$$

The argument φ plays in this relation the role of the generalized reaction coordinate by the continuous change of which the system passes from the initial reactant into the final product. To characterize the nature of the electron reorganization accompanying the transformation of the reactant into the product it is advantageous to use the so-called topological density matrix $\Omega(\varphi)$. Using the procedure described in the previous study¹⁵, the corresponding matrix can be represented in terms of "topological" charge densities $\Omega_{\mu\mu}(\varphi)$ and bond orders $\Omega_{\mu\nu}(\varphi)$ for any arbitrary value of the argument φ . Having determined the corresponding matrices for different values of the argument φ it is now only a matter of straightforward generalization to introduce the topological equivalents of Wiberg indices w and valencies v (Eq. (2)), and to study their variation with the change of the argument φ

$$w_{\mu\nu}(\varphi) = \Omega_{\mu\nu}^2(\varphi) \quad (2a)$$

$$v_{\mu}(\varphi) = \sum_{\nu \neq \mu} \Omega_{\mu\nu}^2(\varphi) = \sum_{\nu \neq \mu} w_{\mu\nu}(\varphi). \quad (2b)$$

In the following part the detailed use of the above-defined "topologically active" valencies will be demonstrated on a concrete example of electrocyclic transformations of 1,3-butadiene and 1,3,5-hexatriene to the corresponding cyclic products (Scheme 1). The first step of the analysis requires a proper description of the structure



SCHEME 1

of the reactants and the products. For this purpose we shall use the bonding functions constructed from the usual HMO molecular orbitals even if the simpler approach describing the structure of the corresponding skeletons, similarly as in the original overlap determinant method, in terms of localized bonds could be used as well. Starting from these bonding functions Φ_R and Φ'_R , the product function has to be transformed, according to the reaction mechanism, into the modified function Φ_P by using the assigning tables. The next step consists then in the determination of

the corresponding density matrices $\Omega(\varphi)$. Since the construction of these matrices has been described¹⁵, it is not necessary to demonstrate the entire procedure in this paper. Let us therefore proceed directly to the discussion of the changes in the valencies during the transformations. The calculated values of the "topologically active" valencies for the reactions studied are summarized in Tables I and II for both the allowed and forbidden transformations. On the basis of these values it is then possible to discuss, similarly as in the original paper by Jug and Gopinathan¹², some general features of the studied transformations. For this purpose use will be made of both the valencies $v_\mu(\varphi)$ of individual atoms and the total valency changes ΔV characterizing the corresponding variations from the global point of view (Eq. (3)) (N denotes the number of the atoms in the system)

$$\Delta V(\varphi) = N - \sum_{\mu}^N v_{\mu}(\varphi). \quad (3)$$

First, the values in the two tables imply that for the reactants and the products the topological valencies of all the carbons reach the limiting value 1. Translated into the classical language, these values correspond to just one bond in which each of the

TABLE I

Values of individual v_i and total (ΔV) "topologically active" valencies for the conrotatory and disrotatory butadiene cyclisation in dependence on the value of the generalized reaction coordinate φ

Valency	Angle						
	0	15	30	45	60	75	90
conrotation							
v_1	1.0	0.973	0.939	0.926	0.939	0.973	1.0
v_2	1.0	0.973	0.939	0.926	0.939	0.973	1.0
v_3	1.0	0.973	0.939	0.926	0.939	0.973	1.0
v_4	1.0	0.973	0.939	0.926	0.939	0.973	1.0
ΔV	0.0	0.108	0.244	0.296	0.244	0.108	0.0
disrotation							
v_1	1.0	0.819	0.458	0.277	0.458	0.819	1.0
v_2	1.0	0.931	0.792	0.723	0.792	0.931	1.0
v_3	1.0	0.931	0.792	0.723	0.792	0.931	1.0
v_4	1.0	0.819	0.458	0.277	0.458	0.819	1.0
ΔV	0.0	0.500	1.500	2.000	1.500	0.500	0.0

carbons is involved in the irreducible core. An interesting insight into the intimate process of structural reorganization can be obtained by the inspection of the variation of both individual and total valencies with the change of the argument φ . As the values in the two tables reveal, the picture of the atomic valency variation is qualitatively similar for both the allowed and forbidden reactions. Despite this overall similarity, there is nevertheless an important quantitative difference indicated by the more profound changes in the case of forbidden reactions. In this connection it is also interesting to note that the individual valency variations are usually much deeper for the terminal atoms of the skeleton between which the new bond starts to be formed. The more substantial changes in the valencies of all individual atoms in the forbidden reactions manifest themselves also by greater changes in the values of the total valency ΔV which for the critical structure corresponding to $\varphi = \pi/4$ attain values approaching closely or equalling exactly 2. On the other hand, for the allowed reactions the ΔV values are much lower. The fact that these values agree not only qualitatively but also quantitatively with the results of the detailed quantum

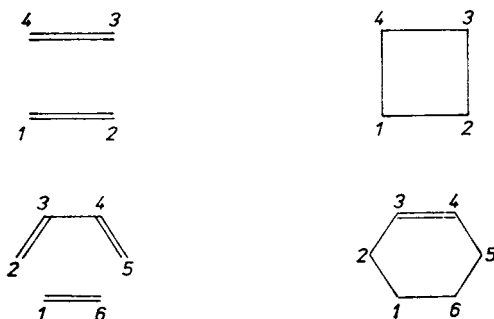
TABLE II

Values of individual (v_i) and total (ΔV) "topologically active" valencies for the conrotatory and disrotatory cyclization of 1,3,5-hexatriene to 2,4-cyclohexadiene in dependence on the value of the generalised reaction coordinate φ

Valency	Angle						
	0	15	30	45	60	75	90
conrotation							
v_1	1.0	0.837	0.512	0.349	0.512	0.837	1.0
v_2	1.0	0.933	0.802	0.735	0.802	0.933	1.0
v_3	1.0	0.972	0.918	0.891	0.918	0.972	1.0
v_4	1.0	0.972	0.918	0.891	0.918	0.972	1.0
v_5	1.0	0.933	0.802	0.735	0.802	0.933	1.0
v_6	1.0	0.837	0.512	0.349	0.512	0.837	1.0
ΔV	0.0	0.516	1.768	2.025	1.768	0.516	0.0
disrotation							
v_1	1.0	0.955	0.894	0.870	0.894	0.955	1.0
v_2	1.0	0.966	0.920	0.901	0.920	0.966	1.0
v_3	1.0	0.986	0.967	0.959	0.967	0.986	1.0
v_4	1.0	0.986	0.987	0.959	0.967	0.986	1.0
v_5	1.0	0.966	0.920	0.901	0.920	0.966	1.0
v_6	1.0	0.955	0.894	0.870	0.894	0.955	1.0
ΔV	0.0	0.186	0.438	0.540	0.438	0.186	0.0

chemical study by Jug and Gopinathan not only confirms their conclusions concerning the biradical nature of the transition states in forbidden reactions^{12,15,17} but it also provides a justification for the proposed incorporation of the valency concept into the framework of the topological approach.

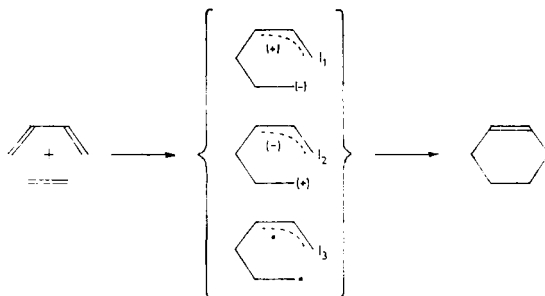
The patterns for other types of pericyclic transformations are entirely analogous. Out of a number of such reactions, cycloadditions represented by the simple model cases of ethene dimerization and the Diels–Alder reaction will be discussed for illustration (Scheme 2). The calculated valencies of the individual atoms in depen-



SCHEME 2

dence on the variation of the reaction coordinate φ for both the $s + s$ and $s + a$ reaction mechanisms are shown in a graphical form in Figs 1 and 2. The conclusions that can be drawn from these plots are to a great extent analogous to what has been found for the above electrocyclic reactions. In particular, it is clear again that for the reactants and the products the valencies of the individual atoms are equal to limiting value of 1. The reaction is then again in all cases characterized by such changes in the individual valencies that the most marked variations are observed for critical structures corresponding to $\varphi = \pi/4$, and these changes are again generally higher for the forbidden reactions. Interesting conclusions follow also from a comparison of the total valency changes ΔV , which in the case of the forbidden $s + s$ ethene dimerization attain a value of 2, indicating thus the biradical nature of the corresponding critical structure^{12,15,17}. The situation is more complicated in the case of the concerted $s + s$ mechanism of the Diels–Alder reaction which, as indicated by both the individual and total valencies, seems to be more advantageous than the forbidden $s + a$ mechanism but nevertheless the corresponding value of ΔV is also close to 2 ($\Delta V = 1.905$). This implies, provided that the Jug–Gopinathan criterion is valid, that the corresponding transition state or intermediate also possesses a considerable biradical character. Since our aim in this study is not to elucidate the mechanism of the Diels–Alder reaction, we do not comment on this result;

instead, we attempt to show to what conclusions the applied topological approach leads in case that the reaction proceeds *via* a nonsymmetrical biradicaloid intermediate advocated by Dewar¹⁸⁻²⁰ rather than by a synchronous concerted mechanism.



SCHEME 3

Since our version of the program for the construction of the topological density matrix is so far capable of handling only closed shell molecules, our analysis will be restricted to the discussion of the zwitterionic intermediates I₁ and I₂ (Scheme 3). Detailed calculations indicate that in the symmetrical case of the ethene to butadiene

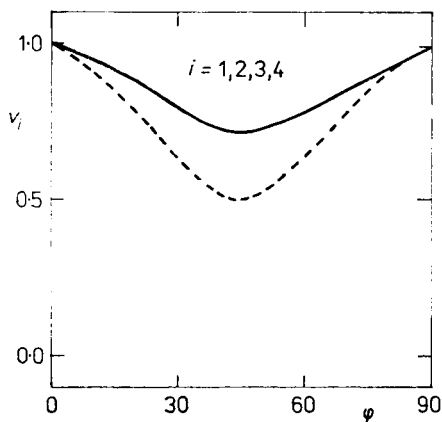


FIG. 1

Dependence of "topologically active" valencies v_i for the concerted thermally allowed $s+a$ (full line) and forbidden $s+s$ (broken line) mechanism of the ethene dimerization on the magnitude of the reaction coordinate φ

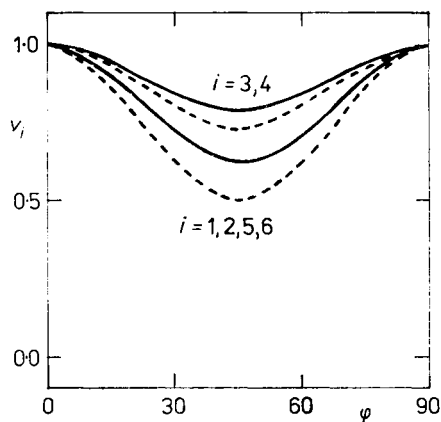


FIG. 2

Dependence of "topologically active" valencies v_i for the concerted thermally allowed $s+s$ (full line) and forbidden $s+a$ (broken line) mechanism of the Diels-Alder reaction on the magnitude of the reaction coordinate φ

addition the two alternative intermediates behave in an entirely identical fashion from the point of view of both the valency and the topological density matrix. The results of the analysis are presented in a graphical form in Fig. 3, demonstrating the dependence of the valencies of individual atoms on the change of the reaction coordinate φ . Since the shape of the curves differs considerably from the simple picture for the synchronous concerted transformation, we consider it worthwhile to comment on at least some of its basic features. First, it is again apparent that in the case of the reactant and the product, the valencies of all individual atoms are identically equal to 1. This result does not hold, however, for the intermediary zwitterions, where the calculations for both I_1 and I_2 indicate a decrease in the active valency at atoms 3 and 5 (terminal atoms of the allylic fragment) to a value of $v = 0.75$. On the other hand, for atom 6 which in the corresponding intermediates bears a localized positive or negative charge, the topologically active valency is identically equal to zero. As a result, the transformation of the reactants into the intermediates is accompanied by a decrease in the total valency by 1.5. This value thus may serve as a criterion indicating the presence of zwitterionic intermediates. The validity of this simple topological criterion is also confirmed by the detailed quantum chemical calculations by Jug²¹, who found values of ΔV close to the "theoretical" value of 1.5 for a number of typically zwitterionic structures. Another important feature revealed

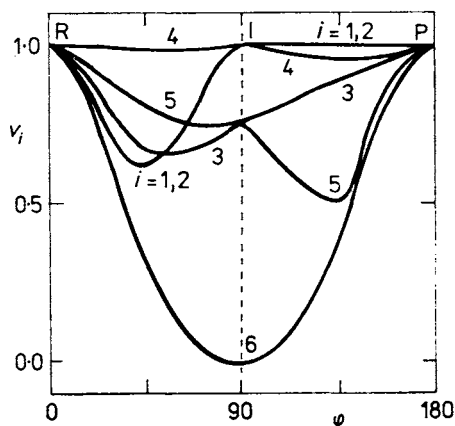


FIG. 3

Dependence of "topologically active" valencies v_i for the nonconcerted mechanism of the Diels-Alder reaction proceeding according to Scheme 3 via the zwitterionic intermediates I_1, I_2 on the magnitude of the reaction coordinate φ

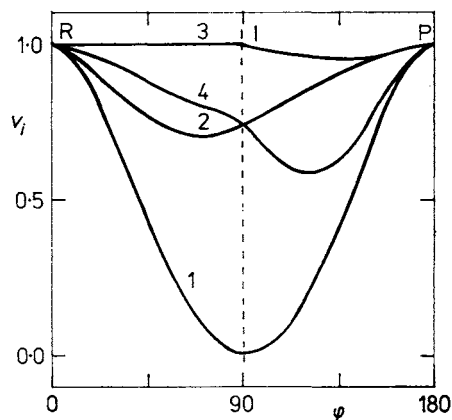


FIG. 4

Dependence of "topologically active" valencies v_i for the nonconcerted thermally forbidden disrotatory cyclization of butadiene proceeding via the nonsymmetrical biradicaloid intermediate, on the value of the generalised reaction coordinate φ

by Fig. 3 is the minimal change in the valency at atom 4 (the central atom of the allylic fragment), for which the corresponding values in either step of the reaction are very close to unity. Instructive and from the chemical point of view easily comprehensible is also the form of the dependence of the valencies of atoms 1 and 2, between which the bond is formed in the first step of the reaction. As a consequence, the form of the dependence in the region of $0 - \pi/2$ is the same as in the above example of concerted reactions. After the formation of this bond in the first step, no topologically important changes occur between atoms 1 and 2, so that within the region of $\pi/2 - \pi$ the values of the corresponding valencies do not vary and identically equal the limiting value of unity. Thus, in addition to atoms 1, 2, 6, deeper valency changes take place also at atoms 3 and 5, and the particular form of these dependences reflects the specific features of the charge distribution and its change at the terminal atoms of the allylic fragment. In this connection it should be noted that the above picture of valency changes does not hold for the specific case of the nonsynchronous Diels–Alder reaction solely but its scope is probably more general. This feeling is supported by the perfect analogy of Fig. 3 with Fig. 4 which describes the nonsynchronous disrotatory cyclization of butadiene to cyclobutene proceeding *via* the nonsymmetrical biradicaloid intermediate by the mechanism proposed on the basis of MINDO calculations by Dewar²².

CONCLUSIONS

All the above examples conclusively demonstrate that by incorporating the original Jug and Gopinathan approach into the framework of the recently proposed topological description of chemical reactivity, the use of the overlap determinant method is enriched with a new aspect — a simple and chemically instructive characterization of structural transformations. This, together with the numerical simplicity of the treatment, makes the suggested generalization a simple and attractive tool for the description of structural transformations as well as for a theoretical discussion of possible mechanisms of chemical reactions.

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