

THE LEAST MOTION PRINCIPLE, CONCERTEDNESS AND THE MECHANISMS OF PERICYCLIC REACTIONS. A SIMILARITY APPROACH

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The recently proposed topological criterion of concertedness was complemented by a procedure allowing the variational determination of reaction paths characterizing the detailed course of bonding reorganization in modified More O'Ferrall diagrams. The proposed approach, allowing the simple unequivocal classification of reaction mechanisms is demonstrated with examples of several selected pericyclic reactions, both forbidden and allowed. The mechanistic conclusions obtained are in qualitative agreement with the predictions based on expectations from Woodward-Hoffmann rules and independent theoretical calculations.

Some time ago we have introduced a new universal criterion allowing a simple and unequivocal classification of mechanisms of pericyclic reactions in terms of concertedness and/or nonconcertedness¹. The criterion is based on simple topological model joining the formalism of the overlap determinant method² with the philosophy of the technique of More O'Ferrall diagrams³. Using this approach we demonstrated that the set of structures lying "inside" the corresponding More O'Ferrall diagrams can be dissected into disjunct classes¹ in such a way that the elements of individual regions are structurally equivalent to either reactant, product or intermediate¹. On the basis of this dissection a criterion was introduced, according to which the reaction is classified as concerted if the reaction path, characterizing the course of the reaction in the More O'Ferrall diagram, passes from the region of the reactant into the region of the product without entering into the region of the intermediate. If, on the other hand, the region of the intermediate is involved, the reaction is classified as nonconcerted.

The practical use of the criterion is conditioned by the knowledge of the reaction path whose determination was not, however, specified in the original study*. Our aim

* An analogous partitioning was reported also for PE hypersurface, where the concept of the so-called catchment regions was introduced by Mezey^{4,5}.

in this study is just to complement the above criterion of concertedness by a procedure allowing the reaction path to be determined.

THEORETICAL

Since the procedure we are going to present is entirely new and original, we consider it convenient to recapitulate briefly the basic ideas on which our considerations are based. The methodological basis of the proposed approach originates from our previous theoretical studies⁶⁻⁹ dealing with the quantitative characterization of the extent of electron reorganization, which is a basic quantity expressing the ease of chemical reactions in terms of the so-called least motion principle (LMP)^{10,11}. The studies⁶⁻⁹ in which the well-known Woodward-Hoffmann rules¹² were alternatively reproduced play a decisive role in this connection. Using this approach we demonstrated that in harmony with the intuitive expectation of LMP, the extent of electron reorganization is generally lower for allowed reactions than for the forbidden ones.

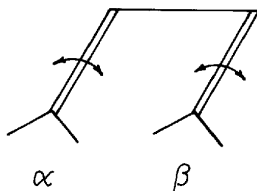
Even if the possibilities of the above approach in rationalizing the various aspects of pericyclic reactivity are very broad indeed, there is nevertheless a certain limitation in the fact that the formalism was in these cases designed only for ideally synchronous concerted reactions, where reactant R is converted into product P in one elementary step (Eq. (1a)) or in contrast for purely asynchronous stepwise mechanism involving the appropriate intermediate (Eq. (1b)).



Such a picture of the reaction mechanism is, however, slightly idealized, since the above two mechanisms represent only certain limiting situations whereas in the majority of real cases, the synchronization in the process of creation and scission of bonds is probably only partial. This implies that the original idealized scheme of strictly distinguishable reaction mechanisms ((1a) vs (1b)) must be replaced by a more realistic picture of various reaction paths differing in the degree of synchronization of bonding changes. An example would be, e.g., the elimination reactions in which the existence of reaction mechanisms corresponding to neither pure concerted E2 nor the stepwise E1 and E1cB mechanisms was assumed rather frequently^{3,13}.

For the visualisation of these general reaction paths the technique of the More O'Ferrall diagrams can be conveniently used. Since this technique has become the basis of the recently proposed topological criterion of concertedness¹ which is the immediate basis for this study, we consider it convenient to recapitulate briefly the principles on

which the method is based. The basic idea of this technique can be best demonstrated on reactions, the course of which is governed by the variations in two nuclear coordinates ρ_1 , ρ_2 represented by, e.g., the lengths of newly created bonds or by some appropriately selected angles describing the process of creation or the rupture of the ring in the cyclic compounds. An example is the cyclization of butadiene to cyclobutene, for which these coordinates are represented by the rotational angles α , β at the terminal carbons of butadiene skeleton (Scheme 1).



SCHEME 1

If the reaction mechanism is regarded classically as a sequence of consecutive processes of scission of old and formation of new bonds, the course of the reaction can be visualized as a line (corresponding to a reaction path) connecting the reactant and the product in a schematic diagram – the so-called More O'Ferrall diagram, where the degree of formation of the bonds is evaluated on individual axes Q_1 , Q_2 by a conventional scale ranging from zero to unity (Fig. 1). It is apparent that the concerted process characterized by the ideal synchronization in the formation of bonds will be described by a diagonal line connecting two opposite corners. The second limiting case of ideal asynchronization can be described by a two-step line going along the periphery and involving the corners with the coordinates $[0,1]$ and $[1,0]$ which correspond to inter-

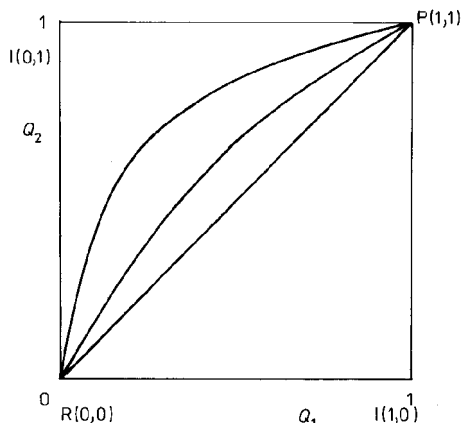


FIG. 1

Schematic representation of reaction paths in More O'Ferrall diagram

mediates. Between these two extremes there is then a practically continuous scale of various intermediate cases corresponding to general situations where the bonding synchronization is only partial. Such a concept of reaction path as a trajectory describing the detailed course of synchronization in the process of scission and the formation of bonds is also the basis of the proposed generalization of the LMP. Such a generalization is based on the introduction of appropriate quantities allowing to characterize the extent of electron reorganization along the general arbitrary reaction path. On the basis of these quantities, the best LMP satisfying reaction path is then determined variationally from the condition of minimization of electron reorganization.

Prior to a detailed presentation of the criterion allowing the corresponding reaction paths to be determined, it is necessary to mention also some conceptual differences differentiating the LMP concept of reaction path from the usual quantum chemical interpretation based on the concept of potential energy hypersurface. The most striking difference concerns the fact that in contrast to usual quantum chemical model of IRC as a trajectory in the configuration space of nuclei, our model of reaction path operates with a classical chemical picture of reaction mechanism as a sequence of electron shifts depicting the gradual scission and formation of individual bonds. For that reason it would probably be difficult to make any straightforward comparison of both approaches, and even if we believe that some parallels do exist, their disclosure is a matter of future systematic investigations, e.g., along the lines of Bader's reconciliation of the quantum chemical and classical picture of chemical structure¹⁴.

Based on this introductory presentation of the philosophy of the proposed approach, let us now proceed to a discussion of the mathematical part of the whole approach. The basis of the proposed model is a simple intuitive idea regarding a chemical reaction as a certain transformation that converts, via a continuous change of a certain parameter, the structure of the reactant into the structure of the product. This concept, based on the recently introduced topological approach known as the method of the overlap determinant^{2,15}, can be mathematically described by Eq. (2), where Ψ_R and Ψ_P are approximate electron wave functions of the reactant and the product, respectively, and where the parameter governing the structural transformation is the variable φ which ranges from 0 to $\pm\pi/2$ *

$$\Psi(\varphi) = \frac{1}{N(\varphi)} (\Psi_R \cos \varphi + \Psi_P \sin \varphi). \quad (2)$$

This simplest model, however, is not appropriate for our purposes since it depicts only a strictly concerted process (*Ia*). If we want to include also the case of a general reac-

* The necessity of allowing the variation of φ within the range 0, $-\pi/2$ is required, as demonstrated in the recent study¹⁶, for the correct description of forbidden reactions.

tion path, the original Eq. (2) must be properly generalized. In the simplest case of a processes which can be described by More O'Ferrall diagrams, such a generalization can be simply depicted by Eq. (3)

$$\Phi(\vartheta, \varphi) = \frac{1}{N(\vartheta, \varphi)} (\cos \vartheta \cos \varphi \Psi_R + \cos \vartheta \sin \varphi \Psi_P + \sin \vartheta \Psi_I), \quad (3)$$

where the corresponding intermediate participates via the approximate wave function Ψ_I and where the possible asynchronicity of the reaction path is given by the parameter $\vartheta = \vartheta(\varphi)$ ($\vartheta \in -\pi/2, \pi/2$).

In connection with Eq. (3), yet another important difference differentiates our approach from usual quantum chemical analyses of reaction mechanisms. This difference concerns the fact while a quantum chemical approach is in principle independent of any external information (all participating species appear automatically as various critical point on the PE hypersurface), in our model which is more closely related to classical chemical ideas, some auxiliary information about the structure of participating molecular species is required. This usually represents no problem with the reactants and the products since their structure is normally known, but certain complications may appear in the case of intermediates. This complication is not, however, too serious since in many cases the structure of the intermediate can be reasonably estimated either from some experimental or theoretical data or on the basis of chemical intuition. Thus, e.g., in the case of pericyclic reactions which are of primary concern for us here, the corresponding intermediates are generally believed to correspond to biradical or biradicaloid species with the eventual contributions of zwitterionic structures in polar cases¹⁷.

Assuming that in a given case the structure of all participating molecular species is known, it is possible to begin the practical exploitation of Eq. (3) and aim at the variational formulation of the LMP. For this purpose it is first necessary to introduce the first order density matrix $\rho(\vartheta, \varphi|\mathbf{x}_1)$ by the relation (4),

$$\rho(\vartheta, \varphi|\mathbf{x}_1) = N \int \Phi^2(\vartheta, \varphi) d\xi_1 \dots d\xi_N d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (4)$$

where \mathbf{x}_i denotes the position vector of the i -th electron, ξ_i its spin coordinate and N the total number of electrons. Using this matrix the differences in the electron configurations of two different structures corresponding to different values of parameters ϑ, φ (e.g. ϑ, φ and ϑ', φ') can be quantitatively characterized by the similarity index K (Eq. (5))

$$K = \frac{\int \rho(\vartheta, \varphi|\mathbf{x}_1) \rho(\vartheta', \varphi'|\mathbf{x}_1) d\mathbf{x}_1}{\left(\int \rho^2(\vartheta, \varphi|\mathbf{x}_1) d\mathbf{x}_1 \right)^{1/2} \left(\int \rho^2(\vartheta', \varphi'|\mathbf{x}_1) d\mathbf{x}_1 \right)^{1/2}}. \quad (5)$$

Expressing the individual density matrices in the basis of atomic orbitals (Eq. (6))

$$\rho(\vartheta, \varphi | \mathbf{x}_1) = \sum_{\mu} \sum_{\nu} [\Omega(\vartheta, \varphi)]_{\mu\nu} \chi_{\mu}(\mathbf{x}_1) \chi_{\nu}(\mathbf{x}_1) \quad (6)$$

and using the same topological approximation as in the previous study⁸, the above general expression for K can be written in the form (7),

$$K = \frac{\text{Tr } \Omega(\vartheta, \varphi) \Omega(\vartheta', \varphi')}{[\text{Tr } \Omega^2(\vartheta, \varphi)]^{1/2} [\text{Tr } \Omega^2(\vartheta', \varphi')]^{1/2}}, \quad (7)$$

from which the relation between the magnitude of K and the differences in the electron configurations of corresponding structures is apparent. It is possible to see that the maximal value of unity attains this index for two identical structures ($\vartheta' = \vartheta$, $\varphi' = \varphi$), and with the increasing deviations of both structures its value monotonously decreases.

The use of this index for the formulation of the least motion principle arises from the following simple idea. Let us assume that we are on a reaction path in a point characterized by the wave function $\Phi(\vartheta', \varphi')$, and we are looking for such an infinitesimally close structure $\Phi(\vartheta, \varphi)$ for which the transformation $\Phi(\vartheta', \varphi') \rightarrow \Phi(\vartheta, \varphi)$ requires a minimal change in the electron configuration. This condition is equivalent to a search for the direction along which the derivative of K at the point $\vartheta' = \vartheta$ and $\varphi' = \varphi$ will attain its minimum. This directional derivative can be mathematically described as (8),

$$\frac{dK}{dl} = \mathbf{s}_{\vartheta} \nabla_{\vartheta} K + \mathbf{s}_{\varphi} \nabla_{\varphi} K, \quad (8)$$

where dl is the length element, ∇_{ϑ} and ∇_{φ} denote components of the gradient, and \mathbf{s}_{ϑ} , \mathbf{s}_{φ} are unit vectors characterizing the corresponding direction. The direct calculation of the gradient of the index K demonstrates, however, that

$$(\nabla_{\vartheta} K)_{\vartheta'=\vartheta}^{\varphi'=\varphi} = 0 \quad (9a)$$

$$(\nabla_{\varphi} K)_{\vartheta'=\vartheta}^{\varphi'=\varphi} = 0. \quad (9b)$$

This implies that there is no direction along which the limiting first derivative of K is nonzero. This suggests that the characterization of the transformation $\Phi(\vartheta', \varphi') \rightarrow$

$\Phi(\vartheta, \varphi)$ is to be based on the second directional derivative (10), which, on the basis of Eqs (9a) and (9b), can be expressed as (11):

$$\frac{d^2K}{dl^2} = \frac{d}{dl} (\mathbf{s}_{\vartheta} \nabla_{\vartheta} K + \mathbf{s}_{\varphi} \nabla_{\varphi} K) \quad (10)$$

$$\left(\frac{d^2K}{dl^2} \right)_{\substack{\vartheta'=\vartheta \\ \varphi'=\varphi}} = (\mathbf{s}_{\vartheta} \mathbf{s}_{\vartheta} \nabla_{\vartheta} \nabla_{\vartheta} K + 2 \mathbf{s}_{\vartheta} \mathbf{s}_{\varphi} \nabla_{\vartheta} \nabla_{\varphi} K + \mathbf{s}_{\varphi} \mathbf{s}_{\varphi} \nabla_{\varphi} \nabla_{\varphi} K). \quad (11)$$

Now taking into account that for $\vartheta' = \vartheta$ and $\varphi' = \varphi$ the index K attains its maximum, then the reaction path satisfying the requirement of minimal changes in electron configurations should continue in the direction along which the corresponding (nonpositive) second derivative is maximal (minimal in absolute value).

Such a criterion for the step by step determination of the reaction path is not, however, entirely satisfactory. The reason for it consists in the local character of the criterion which is not sufficient to ensure that the reaction path starting at the initial reactant will indeed end at the desired product. This suggests that in proposing a satisfactory formulation of the least motion principle, the above local criterion of minimal changes in electron configurations is to be replaced by a global one*. The simplest way to do this consists in introducing a curve integral summing up the contributions of the local second directional derivative along a chosen path in the direction tangential to this path. This integral is given by Eq. (12), where the symbolic limits R and P (reactant and product) correspond, consistent with the Eq. (1), to $\vartheta = 0$, $\varphi = 0$, and $\vartheta = 0$, $\varphi = \pm\pi/2$, respectively:

$$L = \int_R^P \mathbf{s} \nabla \nabla K \mathbf{s} dl. \quad (12)$$

Taking into account that the integral (12) represents a functional the value of which depends on the actual form of the path along which the integration is performed, the "best" reaction path satisfying the requirement of minimal (global) changes in electron configurations can be naturally determined from the variational condition (13), which can thus be regarded

$$\delta L = 0 \quad (13)$$

as the desired general formulation of the least motion principle.

* The necessity of global rather than local formulation of the LMP was already stressed by Igawa and Fukutome¹⁸ and independently also by us (ref.⁷).

The solution of this variational problem can be considerably simplified by taking into account that the reaction path is generally given by the dependence $\vartheta = \vartheta(\varphi)$. This allows the functional (12) to be rewritten symbolically in the form (12) ($\dot{\vartheta} = d\vartheta/d\varphi$), which is well-known from the variational calculus

$$L = \int_0^{\pm\pi/2} f(\vartheta, \dot{\vartheta}, \varphi) d\varphi. \quad (14)$$

Because of the fact that the integrand of Eq. (14) is generally a rather complex function of variables ϑ , $\dot{\vartheta}$, and φ , we did not use the standard procedure based on the integration of corresponding Euler–Lagrange equations in solving the Eq. (13) but, instead an approximate numerical procedure was proposed¹⁹ that allowed the “best” reaction path to be determined by simple selection from a set of “trial” functions approximated in the form of a linear combination (15) of certain “testing functions” $f_k(\varphi)$ that satisfied the boundary condition (16)

$$\vartheta(\varphi) = \sum_k a_k f_k(\varphi) \quad (15)$$

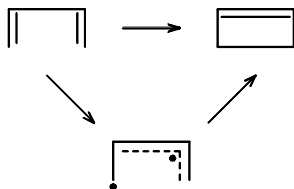
$$f_k(0) = k_k(\pi/2) = 0 \quad (16a)$$

$$|\vartheta(\varphi)| = \pi/2. \quad (16b)$$

Since, however, this procedure is of no direct relevance for the elaboration of the LMP model itself, which was the primary aim of this study, we shall confine ourselves here to the presentation of the final results demonstrating the practical applicability of the approach and the mathematical part of the procedure will be considered in a subsequent publication.

RESULTS AND DISCUSSION

In order to maintain a close correspondence with the previous study¹, in which a new criterion of concertedness was proposed, the entire procedure will first be demonstrated by an example of conrotatory and disrotatory butadiene to cyclobutene cyclization. This allows us to reduce the amount of necessary technical data for which the reference can be found elsewhere^{1,2}. We shall therefore present here only the classical reaction scheme from which the corresponding wave functions Ψ_R , Ψ_P , Ψ_1 can be straightforwardly derived (Scheme 2).



SCHEME 2

For the sake of completeness it should be noticed that, consistent with the topological nature of the method used in the design of the generalized wave function (3), the wave functions Ψ_R , Ψ_P and Ψ_I are of the simple HMO type.

Once the form of the wave functions is specified, the entire subsequent procedure is completely straightforward and consists in the calculation of the density matrix $\rho(\vartheta, \varphi | \mathbf{x}_1)$ and the related similarity index K , on the basis of which the optimal reaction path, that serves for the classification of the reaction mechanism is determined. Such a classification can be very conveniently conducted by use of the above mentioned More O'Ferrall diagrams not only because the visualization of reaction paths it offers is very close to classical chemical thinking but also because of the possibility of exploitation of the recently proposed criterion of concertedness¹, with which this technique is closely connected. The basis of this criterion is the reported finding that the set of structures lying "inside" the corresponding More O'Ferrall diagrams can be dissected into disjunct regions associated with the individual key structures of R, P and I. On the basis of this dissection, the reactions for which the corresponding reaction paths transverse directly from the region of the reactant into the region of the product can be classified as concerted. Where the regions of the intermediate are directly involved, the reaction is to be classified as nonconcerted (Fig. 2). For the above criterion to be used

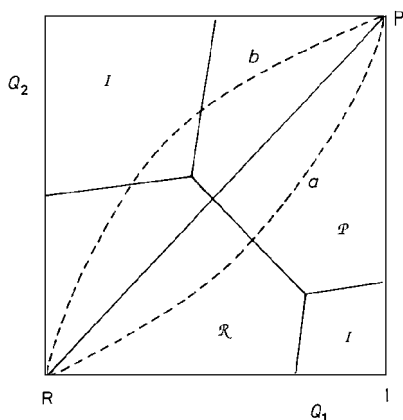


FIG. 2

Schematic classification of reaction mechanisms in terms of partitioning of modified More O'Ferrall diagrams. Line *a* represents asynchronous but concerted process, line *b* nonconcerted process. *R*, *P* and *I* denote the regions of the reactant, product and intermediate, respectively

practically, the reaction path primarily determined in the form of dependence $\vartheta = \vartheta(\varphi)$ must be transformed into the usual More O'Ferrall variables Q_1 , Q_2 and superimposed on the corresponding diagram. The necessary transformation relations are given by Eqs (17), and the resulting pictures of the reaction paths are visualized in Figs 3 and 4:

$$Q_1 = \frac{1}{\pi} (2\varphi + |\vartheta| (1 - \frac{4\varphi}{\pi}) - \vartheta) \quad (17a)$$

$$Q_2 = \frac{1}{\pi} (2\varphi + |\vartheta| (1 - \frac{4\varphi}{\pi}) - \vartheta). \quad (17b)$$

Let us now discuss some basic mechanistic conclusions that can be deduced from the pictures. The first interesting result concerns the comparison of values of the functional L that characterize the extent of electron reorganization along the "best" allowed and forbidden reaction paths. As can be seen, the value of L for an allowed reaction is lower (in absolute value) than for a forbidden one. This confirms the intuitive expectation of LMP that the extent of electron reorganization should be generally lower for allowed reactions than for the forbidden ones. Moreover, these best reaction paths to indeed correspond, in harmony with the conclusions of our previous study¹⁶, to φ varying within $0, \pi/2$ for allowed reactions and within $0, -\pi/2$ for forbidden ones. We thus

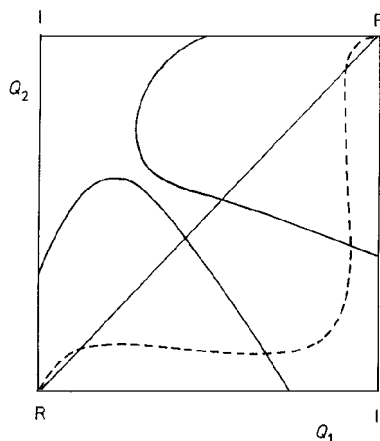


FIG. 3

The partitioning of modified More O'Ferrall diagram with the corresponding reaction path (broken line) for thermally forbidden disrotatory cyclization of butadiene to cyclobutene. The extent of electron reorganization measured by the value of the functional L is -0.48 along this reaction path

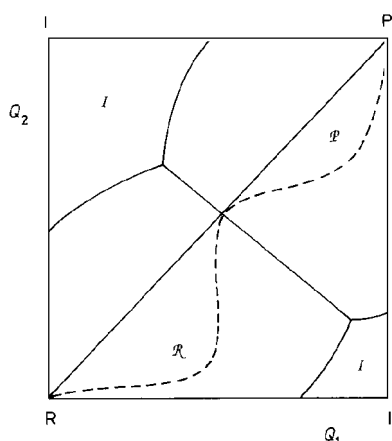


FIG. 4

The partitioning of modified More O'Ferrall diagram with the corresponding reaction path (broken line) for thermally allowed conrotatory cyclization of butadiene to cyclobutene. The extent of electron reorganization measured by the value of the functional L is -0.28 along this reaction path

believe that the basic features of the LMP are apparently well reflected by our model. On the basis of this primary test of the reliability of our approach, it is now, in the second step, possible to begin the discussion of the mechanistic details of both individual reactions. The most interesting in this connection is the case of forbidden reaction. The reason for it lies in the specific form of the partitioning of the corresponding More O'Ferrall diagram which implies that no reaction path can transverse from the region of the reactant into the region of the product without avoiding the region of the intermediate. The reaction mechanisms is therefore classified as nonconcerted, and this conclusion is even strengthened by the remarkable asynchronicity of the reaction path suggesting the inherently stepwise nature of the process. This result is very interesting since the above picture of the reaction mechanism seems to fit well not only with the qualitative expectation of Woodward–Hoffmann rules but also with the results of semi-empirical MINDO calculations by Dewar²⁰ and, indirectly, also with the results of more sophisticated newer studies^{21,22}. In these studies the authors report that the symmetrical critical structure corresponding to forbidden disrotatory reaction is not true transition state but the second order saddle point. This implies, however, (according to Murrell and Laidler theorem²³) that there is another asynchronous reaction path of lower energy which could correspond just to what we found.

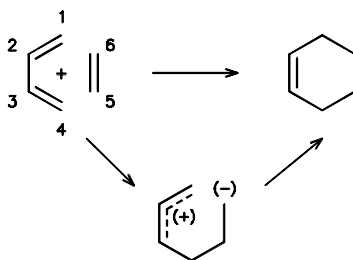
In connection with this remarkable parallel it is, however, necessary to realize that in contrast to direct quantum chemical analyses allowing the localization of the eventual intermediate as a minimum on the PE hypersurface, our approach is much more qualitative and all that we are able to detect is the asynchronicity of the reaction path (stepwise nature of the process). Any closer estimate of the stability of the intermediate is of course out of the scope of our approach. This, however, represents no serious restriction since in a situation where even the “state of the art” *ab initio* calculations are frequently insufficient to provide any definitive answer^{24,25} it is probably not reasonable to insist too much on the numerical values and a simple qualitative picture provided by our model can be quite satisfactory.

As an additional example let us discuss the closely related case of the allowed conrotatory cyclization for which the resulting reaction path is given in the Fig. 4. Here it is possible to see that because of the standard form of the dissection, the reaction mechanism could in principle be both concerted and nonconcerted, and the final decision is therefore conditioned by the knowledge of the actual reaction path. As can be seen from Fig. 4, the actual calculations again confirm the qualitative prediction of Woodward–Hoffmann rules and the reaction is to be classified as concerted even if, surprisingly, the path itself is not ideally synchronous. In this connection it is, however, interesting to remark that despite asynchronicity of the path itself, the critical structure representing the point where the system passes from the region of the intermediate into the region of the product is very close to ideal synchronicity required for this allowed reaction by the Woodward–Hoffmann rules.

In a similar way it would now be possible to analyse the mechanism of any other pericyclic reaction, provided the structure of the intermediate is known with sufficient reliability. This requirement can probably be satisfied for the reactions of parent unsubstituted systems where, owing to low polarity of the system, the intermediate can be reasonably approximated by biradical structures. A slightly more complex situation can occur, however, in the case of substituted skeletons where the substituent induced polarity may increase the contributions of zwitterionic structures. The proposed model is, nevertheless, formulated quite generally so that it can be applied to any biradicaloid intermediate described (in the sense of Salem and Rowland theory¹⁷), by the wave function (18) in the form of a linear combination of two zwitterionic and one biradical structures

$$\Psi_1 = a \Psi_{Z_1} + b \Psi_{Z_2} + c \Psi_B. \quad (18)$$

This opens the possibility of the systematic investigation of pericyclic reactions not only for the model cases of the parent systems but the inclusion of zwitterionic contributions also enables the analysis of eventual mechanistic changes induced in the parent systems by the polar substitution. As an example let us demonstrate the analysis of the mechanism of the push-pull substituted Diels-Alder reaction, where the diene component is substituted in position 1 by donor and dienophilic component in position 6 by the acceptor substitution (Scheme 3).



SCHEME 3

In order to avoid the problems with the relative weights of individual limiting structures of the intermediate (Eq. (18)), the α integrals modelling the substitution in the HMO wave functions of all individual structures were arbitrarily set to $\alpha_D = 3\beta$, $\alpha_A = -3\beta$, so that there is sufficient polarity in the system to secure that the intermediate can be approximated by the pure zwitterionic structure Z_1 . The resulting More O'Ferrall diagram corresponding to the allowed $s + s$ reaction mechanism is given in Fig. 5. The most important feature of this diagram is that, after nearly synchronous approach at the initial stage of the reaction, the reaction path becomes considerably asynchronous and hits the region of the intermediate. This suggests that the reaction mechanism of such a

process should be classified as nonconcerted and stepwise. This result is again very interesting, since even if the mechanism of the parent Diels–Alder reaction is still the focus of the discussion, a majority of both theoretical calculations^{26,27} and experimental data^{28,29} in substituted systems are rather consistent with a stepwise nature of the process, which just corresponds to what we have found.

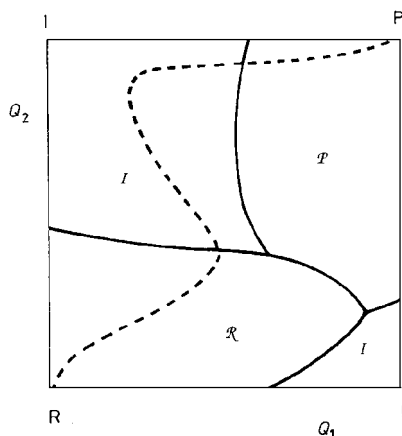


FIG. 5

The partitioning of modified More O'Ferrall diagram with the corresponding reaction path (broken line) for the allowed $s + s$ Diels–Alder cyclization of 1-substituted butadiene with substituted ethene. The extent of electron reorganization measured by the value of the functional L is -0.34 along this reaction path

Summarizing the above results we would like to express our belief that in spite of its simplicity, the proposed LMP model correctly reflects the principal factors governing the details of structural transformations in pericyclic reaction and that its future systematic use can be of considerable help in the qualitative rationalization and the understanding of the mechanistic behaviour of this important class of processes.

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