
**TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY.
ON THE POSSIBLE USE OF SIMILARITY INDEX IN CHARACTERIZING
THE TRANSITION STATE STRUCTURE IN CONCERTED
PERICYCLIC REACTIONS**

Robert PONEC

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát*

Received June 12th, 1986

The use of the topological similarity index as a simple means for classification and characterization of the structure of the transition states in concerted pericyclic reactions is discussed. The suggested formulation makes it possible to bring a quantitative aspect into the empirical Dewar's classification of transition states in terms of aromaticity and/or antiaromaticity.

Although recent theoretical works¹ indicate that transition states can in principle be characterised experimentally, such a direct information on their structure is as yet practically unavailable and in its obtaining we have to resort to either quantum chemical calculations or to some qualitative concepts based, *e.g.*, on the orbital symmetry conservation principle² or the McIver's analysis of symmetry properties of critical points on the potential energy hypersurface³. These approaches can be, in a certain sense, augmented by the Dewar's classification of transition states in terms of aromaticity and/or antiaromaticity⁴. The conclusions based on the use of these simple methods as well as on direct quantum chemical calculations are, however, frequently contradictory. A typical case, for instance, is the Diels-Alder reaction³⁻¹⁵ where the structure of the transition states still remains open to discussion. Although such cases of discrepancy between the conclusions of different theoretical methods and approaches may lead to a certain skepticism when assessing the reliability of any other criteria related to the structure of the transition states, the present paper is intended to draw the attention to some, so far nonconsidered, topological aspects that, in our opinion, could contribute to the solving of the problem under discussion.

THEORETICAL

The basic idea of the proposed topological approach relies on the recently formulated overlap determinant method¹⁶ and on its generalization to the description of the

electron density reorganization during reactions¹⁷. The detailed course of this reorganization is characterized by the so-called topological density matrix $\Omega(\varphi)$, describing, in dependence on the change of the argument φ , the structure of the general transient species in an arbitrary point of the concerted reaction coordinate. For the analysis of the structure of this species we have recently used description in terms of occupation numbers of "natural orbitals" diagonalizing the density matrix $\Omega(\varphi)$ for different values of the argument φ . This analysis revealed fundamental differences in the nature of the electron density reorganization of allowed and forbidden reactions. The crucial role in this analysis plays the critical structure described by the matrix $\Omega(\pi/4)$.

In the present work some general structural features of this critical species, particularly in relation to its possible identification with the corresponding transition state, will be discussed for a series of examples of pericyclic reactions. This discussion is directly based on the use of the so-called topological index of similarity¹⁸. This index, defined by Eq. (1), was originally introduced

$$r_{RP} = (1/2N) \text{Tr}(P_R \bar{P}_P) \quad (1)$$

for a quantitative characterization of the similarity between the reactant (R) and the product (P) as the starting and final points of the chemical reaction. The normalizing factor $1/2N$ ensures the value of r to vary between 0 and 1 measuring thus the extent of the similarity.

In the framework of the study described in the original paper¹⁸, the density matrices P_R and \bar{P}_P can be regarded as the limiting cases of the topological density matrix $\Omega(\varphi)$ for $\varphi = 0$ and $\varphi = \pi/2$, respectively. This analogy also suggests that Eq. (1) can be generalized to characterize the similarity not only between the reactants and products but between any two structures described by the density matrices $\Omega(\varphi_1)$ and $\Omega(\varphi_2)$ for two different values of the argument φ (Eq. (2))

$$r_{X_1, X_2} = \frac{1}{\mathcal{N}_{\varphi_1 \varphi_2}} \text{Tr}(\Omega(\varphi_1) \Omega(\varphi_2)) \quad (2)$$

This generalization concerns, in particular, the normalizing factor $\mathcal{N}_{\varphi_1 \varphi_2}$ that is no more equal to the universal value of $2N$ but depends on φ_1 and φ_2 values. This is so because in the general case, where φ is different from 0 and $\pi/2$, the bonding function of the $X(\varphi)$ species is described by a combination of the determinants Φ_R and Φ_P rather than by a single determinant. As a consequence, the idempotency relations, leading to the universal normalizing factor $2N$ in Eq. (1), fail to hold. The normalizing factor $\mathcal{N}_{\varphi_1 \varphi_2}$ has to be therefore redefined in a way ensuring the similarity index r_{X_1, X_2} to be unity if two identical structures are compared. This condition can be the most simply satisfied by Eq. (3)

$$\mathcal{N}_{\varphi_1\varphi_2} = \sqrt{\xi_1} \cdot \sqrt{\xi_2} \quad (3)$$

$$\xi_i = \sum_{\mu} \sum_{\nu} [\Omega(\varphi_i)]_{\mu\nu}^2 \quad i = 1, 2.$$

By the choice of different values of the argument φ and, consequently, of corresponding density matrices $\Omega(\varphi)$, the reorganization of the electron density can be characterized from different aspects. One of such possibilities that has some relation to the so-called least-motion principle¹⁹⁻²¹, consists in the fixation of the argument φ_1 at $\varphi_1 = 0$ or $\varphi_1 = \pi/2$ corresponding to the reactant and the product, respectively. By varying φ_2 within the interval $0 - \pi/2$ it is then possible to characterize the similarity between the general species $X(\varphi)$ and the reactant ($r_{RX(\varphi)}$) or the product ($r_{PX(\varphi)}$) in terms of the dependence of $r_{RX(\varphi)}$ or $r_{PX(\varphi)}$ on the generalized reaction coordinate. Such a dependence is schematically shown in Fig. 1.

Let us discuss now general features of this dependence. First it is clear that for $\varphi = 0$, $r_{RX(0)}$ is identically equal to unity because it describes the similarity of the reactant to itself. Then, the $r_{RX(\varphi)}$ value decreases monotonically with increasing φ to attain the minimum r_{RP} at $\varphi = \pi/2$. The situation with the $r_{PX(\varphi)}$ index is analogously reversed, *i.e.*, the maximum and minimum values are attained at $\varphi = \pi/2$ and $\varphi = 0$, respectively. The two curves intersect in the point φ^* where the relation (4) holds, indicating that the

$$r_{RX(\varphi^*)} = r_{PX(\varphi^*)}, \quad (4)$$

similarity between the critical structure $X(\varphi^*)$ and the reactant is the same as the similarity between this structure and the product. From the symmetry of the problem it is clear that such condition is fulfilled for $\varphi^* = \pi/4$, *i.e.*, for the same critical structure as disclosed by the previous analysis on the topological density matrix¹⁷. The Eq. (4) can be therefore interpreted as indicating that the electronic structure

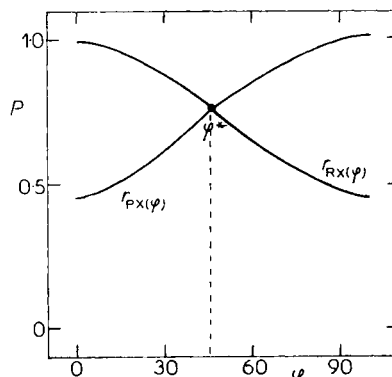


FIG. 1

A schematic dependence of similarity indices $r_{PX(\varphi)}$ and $r_{RX(\varphi)}$ on argument φ . The curves intersect in point φ^*

of the critical species $X(\pi/4)$ is (in some respect) intermediate between the structure of the reactant and the product. This property is, however, ascribed just to the transition state in the classical approach. In the sense of this analogy let us therefore attempt to analyse whether and to what extent it is really possible to identify the critical species $X(\pi/4)$ with the corresponding transition state. For this purpose we shall use a simple methodology based on the comparison of the topological density matrix $\Omega(\pi/4)$ of the critical species $X(\pi/4)$ with the density matrix of certain reference structures selected on the basis of the Dewar's classification⁴. From this point of view it is then possible to expect *e.g.*, that the critical species in six-electron pericyclic transformations should exhibit a high similarity to benzene as a typical representative of "aromatic" transition states. On the other hand, the corresponding critical species in four-electron transformations should approach the structure of the "antiaromatic" cyclobutadiene. The values of the similarity index represent thus a certain objective criterion allowing to select from a number of several alternative structures the one that approaches to the structure of the critical species most closely.

RESULTS AND DISCUSSION

As the simplest example of pericyclic reactions we shall discuss the thermally initiated cyclization of 1,3-butadiene to cyclobutene. Within the scope of the overlap determinant method extended to the molecular similarity problems¹⁸, the structure of the butadiene will be described by a set of HMO π molecular orbitals φ_1, φ_2 whereas the structure of cyclobutene will be treated in terms of localised bonds π_{23}, σ_{14} (Eq. (5))

$$\begin{aligned}\Phi_R &= |\varphi_1 \bar{\varphi}_1 \varphi_2 \bar{\varphi}_2| \\ \Phi_P &= |\pi'_{23} \bar{\pi}'_{23} \sigma'_{14} \bar{\sigma}'_{14}|.\end{aligned}\quad (5)$$

In the next step the bonding function Φ'_P , where the bonds are expressed in the basis of atomic orbitals χ' , has to be transformed into the modified function Φ_P in the basis χ .

The mutual relation of the basis sets χ' and χ is again described by the usual assigning tables (Eq. (6)) the form of which depends on the actual reaction mechanism^{16,17}

conrot	disrot	
$\chi'_1 \rightarrow \chi_1$	$\chi'_3 \rightarrow \chi_3$	$\chi'_1 \rightarrow \chi_1$
$\chi'_2 \rightarrow \chi_2$	$\chi'_4 \rightarrow -\chi_4$	$\chi'_3 \rightarrow \chi_3$
		$\chi'_2 \rightarrow \chi_2$
		$\chi'_4 \rightarrow \chi_4$

(6)

On the basis of these assigning tables modified functions Φ_P^{con} and Φ_P^{dis} can be construc-

ted. These modified functions are then used to set up in the conventional manner, the bonding functions of the general transient species $X(\varphi)$ (Eq. (7))

$$\Phi^\alpha(\varphi) = \frac{1}{N(\varphi)} \{ \cos \varphi \Phi_R + \sin \varphi \Phi_P^\alpha \} \quad (7)$$

$$\alpha = \text{con, dis}$$

and, based on them, the corresponding topological density matrices $\Omega^\alpha(\varphi)$. For the case of $\varphi = \pi/2$ corresponding to the product these matrices are given by Eqs (8)

$$\Omega^{\text{con}}(\pi/2) = \begin{bmatrix} 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \end{bmatrix} \quad (8a)$$

$$\Omega^{\text{dis}}(\pi/2) = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{bmatrix}. \quad (8b)$$

Similarly, for $\varphi = 0$ the matrix $\Omega(0)$ corresponds to the Coulson's charge density-bond order matrix in the butadiene. Expressing with the aid of these matrices the similarity index between the reactant and the product for both alternative reaction mechanisms, one obtains the values given by Eq. (9)

$$\begin{aligned} r_{\text{RP}}^{\text{con}} &= 0.723 \\ r_{\text{RP}}^{\text{dis}} &= 0.500. \end{aligned} \quad (9)$$

Previously we pointed out that there is analogy allowing us to interpret these values in terms of the so-called least-motion principle¹⁸⁻²¹. In its original formulation this principle combines the condition of the easy course of the reaction with the requirement of the minimal changes in the spatial arrangement of the atoms and in the electronic configuration of the reacting molecules.

The above introduced similarity index represents a convenient characteristics just from the point of view of this second, usually neglected condition since its values can be regarded to measure the changes in electron configuration that the least motion principle speaks about.

In the light of the above analogy with the least motion principle it is then clear that the higher is the similarity of two molecules, the smaller reorganization will be necessary to transform one structure into another and, hence, the easier their mutual transformation should be. Thus we see that the similarity index adds a quantitative aspect to the qualitative Woodward-Hoffmann classification.

The determination of the similarity index between the reactant and the product characterizes the given reaction only globally revealing no details on the process of the electronic reorganization. From the need of such a more detailed insight a temptation for further generalization arises. One of the possibilities represents the information resulting from the values of the similarity index between the reactant or product and the critical $X(\pi/4)$ structure. For the cyclisation of butadiene values are given by Eq. (10)

$$\begin{aligned} r_{\text{RX}(\pi/4)}^{\text{con}} &= r_{\text{PX}(\pi/4)}^{\text{con}} = 0.926 \\ r_{\text{RX}(\pi/4)}^{\text{dis}} &= r_{\text{PX}(\pi/4)}^{\text{dis}} = 0.865. \end{aligned} \quad (10)$$

A comparison of these values implies that the attainment of the critical structure in the case of allowed conrotatory cyclization is connected with smaller requirements on the extent of the electronic reorganization than for the forbidden disrotatory reaction. This result thus alternatively supports the conclusions of our previous study¹⁷ and reveals thus the similarity of physical principles lying in the basis of Woodward-Hoffmann rules and the least motion principle.

After this excursus, let us pass to the main goal of this study, the discussion of the general structural features of the critical species $X(\pi/4)$. In the sense of the above general analysis we shall make use of the similarity indices between the critical structure $X(\pi/4)$ and some suitable reference structures. This similarity is quantitatively expressed by the index (11),

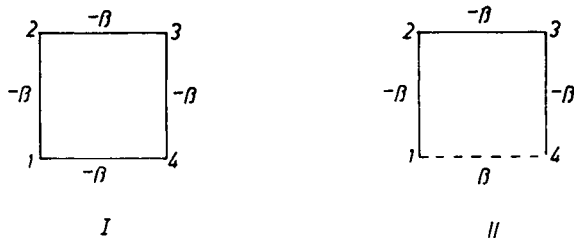
$$r_{\ddagger, \text{ref}} = \frac{1}{N_{\ddagger}} \text{Tr}(\mathbf{\Omega}(\pi/4) \mathbf{\Omega}_{\text{ref}}), \quad (11)$$

where N_{\ddagger} is the normalizing factor and $\mathbf{\Omega}(\pi/4)$ and $\mathbf{\Omega}_{\text{ref}}$ are topological density matrices for the critical and reference structures. For the cyclization of the butadiene, the density matrices of the critical species $X(\pi/4)$ are given by Eq. (12)

$$\mathbf{\Omega}^{\text{con}}(\pi/4) = \begin{pmatrix} 1 & 0.505 & 0 & -0.816 \\ 0.505 & 1 & 0.816 & 0 \\ 0 & 0.816 & 1 & 0.505 \\ -0.816 & 0 & 0.505 & 1 \end{pmatrix} \quad (12a)$$

$$\mathbf{\Omega}^{\text{dis}}(\pi/4) = \begin{pmatrix} 1 & 0.447 & 0 & 0.276 \\ 0.447 & 1 & 0.723 & 0 \\ 0 & 0.723 & 1 & 0.447 \\ 0.276 & 0 & 0.447 & 1 \end{pmatrix}. \quad (12b)$$

In accordance with the Dewar's classification we attempt to compare these structures with cyclobutadiene *I* and Möbius cyclobutadiene *II* as suitable topological models



for the corresponding antiaromatic and aromatic transition states. The actual values of the corresponding similarity indices (13),

$$\begin{aligned}
 r_{\ddagger, I}^{\text{con}} &= 0.737 & r_{\ddagger, I}^{\text{dis}} &= 0.982 \\
 r_{\ddagger, II}^{\text{con}} &= 0.986 & r_{\ddagger, II}^{\text{dis}} &= 0.846,
 \end{aligned}
 \tag{13}$$

clearly confirm the validity of the empirical Dewar's approach indicating moreover near equivalency of the corresponding critical and preferred reference structures. The next step of the analysis consists now in checking the possibility of identification of these structures with transition states. For this purpose it is necessary to confront the conclusions of the above theoretical analysis with the detailed results of quantum chemical calculations on the structure of the reference molecules. In our case such calculations predict cyclobutadiene to exhibit the Jahn–Teller instability^{22,23}. Consequently, the critical intermediate of the disrotatory butadiene cyclisation should probably possess similar structural features. If it is true, the critical species $X^{\text{dis}}(\pi/4)$ does not represent the true saddle point on the corresponding PE hypersurface but rather a structure with two negative eigenvalues of the Hessian matrix. In the light of this analogy which is confirmed also by the results of the recent *ab initio* calculation²⁴, the results of the earlier Dewar's study²⁵ on the structure of transition states in forbidden reactions are natural. Really, if a point of the structural instability such as of Jahn–Teller type lies on the symmetry-conserving reaction coordinate, the system tends to violate the symmetry restrictions and the reaction will proceed along some near-by structurally stable reaction coordinate via an unsymmetrical transition state²⁶.

Another case of electrocyclic transformation on which the use of the suggested formalism will be demonstrated is the cyclization of 1,3,5 hexatriene to 2,4-cyclohexadiene. We will confine ourselves to the presentation of the most important results only. First, the values of the similarity indices between the reactant and the product (14),

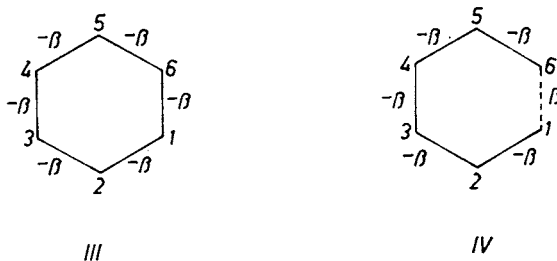
$$\begin{aligned}
 r_{\text{RP}}^{\text{con}} &= 0.658 \\
 r_{\text{RP}}^{\text{dis}} &= 0.759,
 \end{aligned}
 \tag{14}$$

lead again to the same discrimination between the reaction mechanisms as predicted by Woodward–Hoffmann rules as well as by the “integrally” formulated least motion principle. This parallelism appears, however, not only from the integral point of view, but also in the lower demands for the reorganization of the electron density on attaining the critical structure $X(\pi/4)$ in the case of allowed disrotatory cyclization (15)

$$\begin{aligned} r_{RX(\pi/4)}^{\text{con}} &= r_{PX(\pi/4)}^{\text{con}} = 0.917 \\ r_{RX(\pi/4)}^{\text{dis}} &= r_{PX(\pi/4)}^{\text{dis}} = 0.935. \end{aligned} \quad (15)$$

Concerning the structures of the transition states, the values of the corresponding similarity indices confirm again the prediction of the Dewar’s classification requiring for the disrotatory reaction the aromatic transition state isoconjugated with benzene *III* whereas in the case of conrotatory cyclization the critical species displays the similarity to Möbius benzene *IV* (Eq. (16))

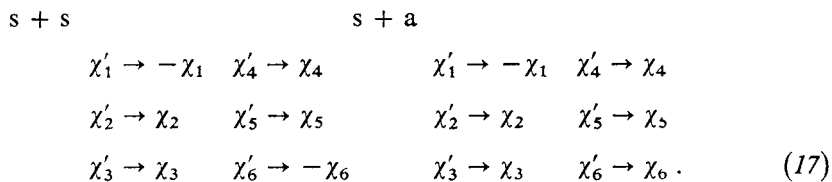
$$\begin{aligned} r_{\ddagger,III}^{\text{con}} &= 0.896 & r_{\ddagger,III}^{\text{dis}} &= 0.992 \\ r_{\ddagger,IV}^{\text{con}} &= 0.973 & r_{\ddagger,IV}^{\text{dis}} &= 0.807. \end{aligned} \quad (16)$$



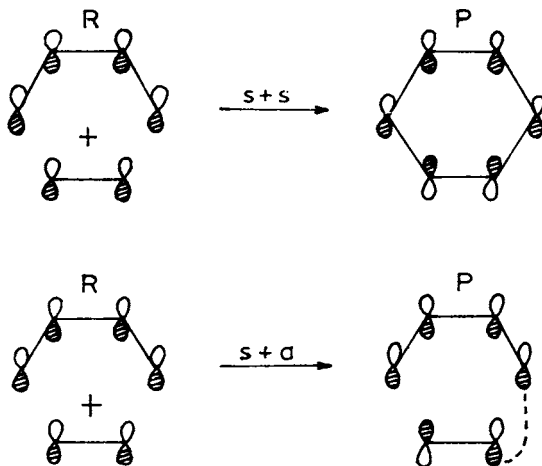
Analogy with the structurally stable benzene suggests that the critical structure of the disrotatory cyclization should correspond to the true transition state, whereas this is not true for conrotatory cyclization because of the Jahn–Teller instability of the Möbius benzene. Thus the transition state for the forbidden conrotatory cyclization will be probably unsymmetrical for the same reasons as in the case of the disrotatory butadiene cyclization.

In the same way we can analyse any other pericyclic reaction. From a number of possible examples we are going to pay particular attention to the so-called Diels–Alder reaction in order to demonstrate how the suggested formalism can, in our opinion, contribute to the solving of the long-existing discussions on the structure of the corresponding transition states. Let the structures of the reacting molecules be described by the bonding functions Φ_R and Φ_P' constructed in a usual way with exception for the butadiene fragment, which is treated again in terms of the HMO π

molecular orbitals. The transformation of the product bonding function Φ_p' from the basis of the atomic orbitals χ' into the basis χ is again described by the assignment tables the forms of which (given by Eq. (17)) are immediately evident from the Scheme 1.



A specific feature of this assignment that has significant consequences for the structures of the transition states in the case of the allowed $s + s$ addition, is a double change in the phase properties of the basis orbitals occurring on centers 1 and 6.



SCHEME 1

What is substantial is that this change is not a mere consequence of the particular choice of the phase properties of the orbitals in Scheme 1 but a consequence of some much deeper reasons connected with the topological structure of the cyclic arrangement of the orbitals basis in the transition state.

After having performed the transformation described by the assigning tables it is possible to construct the bonding function of the general transient species and, based on it, the corresponding topological density matrix of the critical species X ($\pi/4$). Its actual form for the case of the allowed $s + s$ addition is given by Eq. (18)

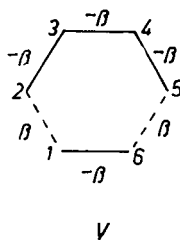
$$\Omega^{s+s}(\pi/4) = \begin{bmatrix} 1 & -0.558 & 0 & 0.071 & 0 & 0.558 \\ -0.558 & 1 & 0.467 & 0 & -0.313 & 0 \\ 0 & 0.467 & 1 & 0.755 & 0 & 0.071 \\ 0.071 & 0 & 0.755 & 1 & 0.467 & 0 \\ 0 & -0.313 & 0 & 0.467 & 1 & -0.558 \\ 0.558 & 0 & 0.071 & 0 & -0.558 & 1 \end{bmatrix}. \quad (18)$$

In discussing the structure of this species it is again possible to use the analogy with the Dewar's classification expecting for the $4s + 2s$ cycloaddition the aromatic transition state isoconjugated with benzene. The calculated values of the similarity index for this type of the reference structure, however, indicate that the critical intermediate substantially differs from the aromatic benzene structure (Eq. (19))

$$\begin{aligned} r_{\ddagger, \text{III}}^{s+s} &= 0.692 \\ r_{\ddagger, \text{III}}^{s+a} &= 0.718. \end{aligned} \quad (19)$$

This indicates that in visualizing the structure of the critical species it will be necessary to refer to another reference structure. From a number of possible alternatives the best one seems to be the hypothetical structure V. The similarity indices (20) really

$$\begin{aligned} r_{\ddagger, \text{V}}^{s+s} &= 0.980 \\ r_{\ddagger, \text{V}}^{s+s} &= 0.842 \end{aligned} \quad (20)$$



show that this model, in which the topology of the cyclic arrangement of the basis orbitals is respected by the change of the sign of two resonance integrals, approaches the structure of the critical species much more closely than benzene. Now, whether this critical structure can or cannot be identified with the transition state depends to a great extent on the structural stability and/or instability of the corresponding reference structures. Unlike the preceding cases, where the problem of the structural stability of the critical species could be simply resolved with the reference to the Jahn-Teller character of the reference structure concerned (cyclobutadiene, Möbius

benzene), the stability of the reference structure V in Diels–Alder reaction requires a detailed analysis. If such analysis proves the structure V to be stable, the transition will be symmetrical as suggested by some *ab initio* calculations, whereas its instability opens the possibility for the unsymmetrical transition state advocated by Dewar^{13–15} and by Ortega⁹.

Being aware of the fact that the results of such analysis may to a considerable extent depend on the reliability of the particular quantum chemical method used, we leave the question of the transition state structure opened. As the most interesting result of this study we therefore consider the methodological advance allowing to transform the problem of the transition state structure into the problem of structural stability of some properly selected reference structures.

REFERENCES

1. Bersuker I. B.: *Nouv. J. Chim.* **4**, 139 (1980).
2. Woodward R. B., Hoffmann R.: *Angew. Chem.* **81**, 797 (1969).
3. McIver J. jr: *Acc. Chem. Res.* **7**, 73 (1974).
4. Dewar M. J. S.: *Angew. Chem., Int. Ed.* **10**, 761 (1971).
5. Townshend R. E., Ramunni G., Segal G., Hehre W. J., Salem L.: *J. Am. Chem. Soc.* **98**, 2190 (1976).
6. Dewar M. J. S., Griffin A. C., Kirchner S.: *J. Am. Chem. Soc.* **96**, 6225 (1974).
7. Brown F. K., Houk K. N.: *Tetrahedron Lett.* **25**, 4609 (1984).
8. Burke L. A., Leroy G., Sana M.: *Theor. Chim. Acta* **44**, 219 (1977).
9. Ortega M., Oliva A., Lluch M. J., Bertran J.: *Chem. Phys. Lett.* **102**, 317 (1983).
10. Basilevský M. V., Shamov A. G., Tikhomirov V. A.: *J. Am. Chem. Soc.* **99**, 1369 (1977).
11. Jug K., Kruger W. H.: *Theor. Chim. Acta* **52**, 19 (1979).
12. Pancíř J.: *J. Am. Chem. Soc.* **104**, 7424 (1982).
13. Dewar M. J. S., Olivella S., Rzepa H. S.: *J. Am. Chem. Soc.* **100**, 5650 (1978).
14. Dewar M. J. S., Pierini A. B.: *J. Am. Chem. Soc.* **106**, 203 (1984).
15. Dewar M. J. S.: *J. Am. Chem. Soc.* **106**, 209 (1984).
16. Ponec R.: *This Journal* **49**, 455 (1984).
17. Ponec R.: *This Journal* **50**, 1121 (1985).
18. Ponec R.: *This Journal* **52**, 555 (1987).
19. Rice F. O., Teller E.: *J. Chem. Phys.* **6**, 489 (1938).
20. Rice F. O., Teller E.: *J. Chem. Phys.* **7**, 199 (1939).
21. Hine J.: *J. Am. Chem. Soc.* **88**, 5525 (1966).
22. Hess B. A., Čársky P., Schaad L. J.: *J. Am. Chem. Soc.* **105**, 695 (1983).
23. Salem L.: *Electrons in Chemical Reactions. First Principles*. Wiley, New York 1982.
24. Breulet J., Schaefer H. F. III.: *J. Am. Chem. Soc.* **106**, 1221 (1984).
25. Dewar M. J. S., Kirchner S.: *J. Am. Chem. Soc.* **96**, 5244 (1974).
26. Murrell J. N., Laidler K. J.: *Trans. Faraday Soc.* **64**, 371 (1968).

Translated by R. Ponec.