TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY. CORRELATION DIAGRAMS AND OVERLAP DETERMINANT METHOD

Robert PONEC

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

Received August 15th, 1985

The recently proposed overlap determinant method is applied as an alternative means of construction of correlation diagrams. In comparison with existing techniques the main advantage of the proposed formalism lies above all in its universality allowing the unified classification of all types of chemical reactions.

Contemporary theory of chemical reactivity is closely connected with the concept of potential energy hypersurfaces. For the purpose of a number of qualitative considerations it is not, however, necessary to know the detailed form of these hypersurfaces but only the knowledge of their most important features is frequently sufficient. These features are generally well reproduced by the so-called correlation diagrams schematically depicting the mutual correspondence of different electronic states of reactants and products of a given reaction.

The first successful attempt to introduce these diagrams into the theory of organic reactivity is due to Longuet-Higgins and Abrahamson[1], who rationalized on their basis the well known Woodward–Hoffmann rules[2] and opened thus the broad possibilities of use not only for thermal and photochemical but also for catalytic reactions[3,4].

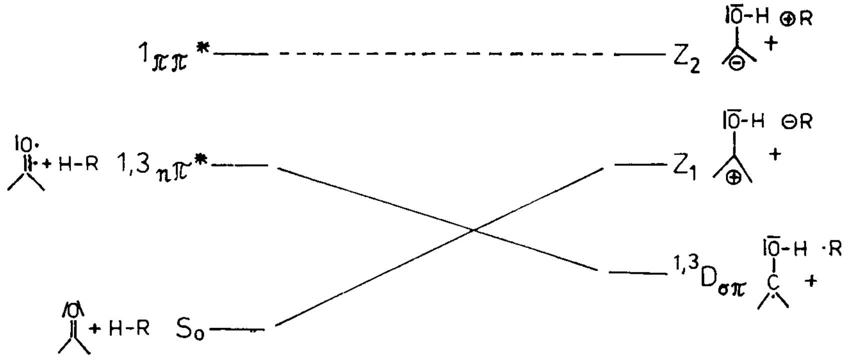
Longuet-Higgins and Abrahamson[1] introduced also a classical technique of construction of state correlation diagrams based on the construction of corresponding orbital diagrams depicting the mutual assignment of individual molecular orbitals of the reactant and the product. Such an assignment requires, however, that both reactant and product possess the same element of symmetry that is conserved in the course of the whole reaction and that moreover satisfies also some additional conditions. These conditions have been shown to be especially restrictive in photochemistry, where the original technique of the construction of the correlation diagrams had to be modified. The elaboration of these modifications is connected with the names of Michl and Salem[5–7] and corresponding the so-called Salem's diagram found the important place in a contemporary theory of photochemical reactivity.

Our aim in this study is to demonstrate the usefulness of the overlap determinant method (ODM) as a simple and efficient tool for the construction of correlation diagrams.

RESULTS AND DISCUSSION

Since the use of overlap determinant method is sufficiently described in the original literature[8,9] it is not necessary to repeat its principles and one may immediately describe only the generalization for the construction of correlation diagrams. Such a generalization is based on a simple idea connecting the condition of direct correlation of electronic states of the reactant and the product with the requirement of allowance of their mutual transformation. In the framework of such approach the correlation diagrams are therefore constructed directly without the intermediation of corresponding orbital correlations and the overlap determinant method is used only as a simple aid to characterize the feasibility of mutual transformation of different electronic states of both reaction partners. The detailed application of this technique will now be demonstrated on a number of examples.

As a first of them let us discuss *e.g.* the construction of the Salem diagram for the photoinitiated H-abstraction by excited carbonyl compounds. The final diagram taken from the original Salem paper[7] (Scheme 1) correlates the $^3n\pi^*$ excited state



SCHEME 1

of the carbonyl component with $^3D_{\sigma\pi}$ biradical state, describing the most stable arrangement of primary products of fragmentation. On the other hand, the ground state of the alkanone correlates with the lowest zwitterionic state Z_1 of the product whereas the second zwitterionic state Z_2 is correlated with the $^1\pi\pi^*$ state of the excited alkanone.

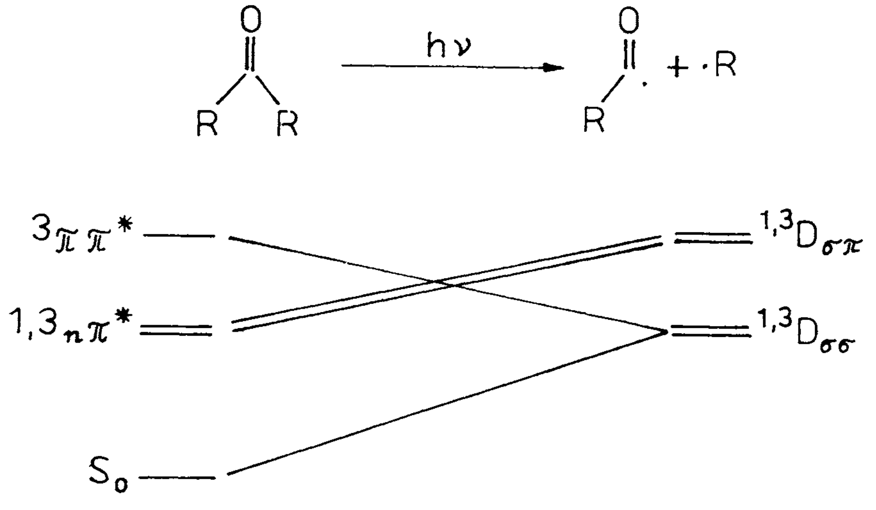
In the following part the detailed use of the overlap determinant method in reproducing these principal features of the Salem diagram will be described.

The case of $^3n\pi^*$ initiated abstraction was analysed in the previous paper[9] and need not be repeated. For the sake of completeness it is nevertheless usefull to notice that the correlation of $^3n\pi^*$ and $^3D_{\sigma\pi}$ is confirmed by the nonzero value of the corresponding overlap determinant. From the remaining correlations the most interesting situation concerns the reaction from the ground state where owing to closed shell character of zwitterionic states one has to take into consideration both possible correlations $S_0 \rightarrow Z_1$ and $S_0 \rightarrow Z_2$. From these two alternatives the overlap determinant method unequivocally selects the correlation with Z_1 state suggested by the original Salem diagram. In the light of the above discussion this preference is confirmed by the nonzero value of the overlap determinant for the reaction $S_0 \rightarrow Z_1$[9] whereas for the alternative reaction $S_0 \rightarrow Z_2$ the overlap determinant equals zero (Eq. (1))

$$D_{S_0 \rightarrow Z_2} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 1 & 0 & 0 \end{vmatrix}^2 = 0 \,. \tag{1}$$

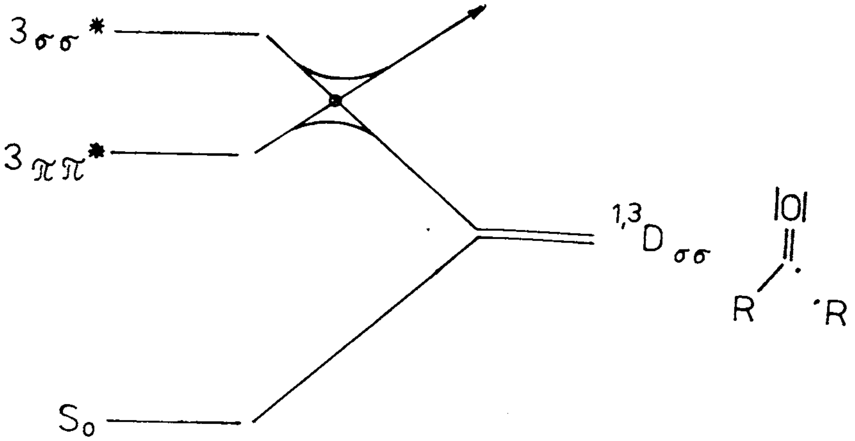
The case of remaining correlation of $^1\pi\pi^*$ state and zwitterionic state Z_2 is more complicated and its satisfactory analysis requires to refer to the important concept of theory of photochemical reactions, the concept of "feasible forbidden reactions"[10]. In order to demonstrate the meaning of this concept let us analyze as a simple example the reaction of the photochemical α-splitting.

The simplified correlation diagram depicting the mutual assignment of several important photoreactive states taken again from the original Salem paper[7] is presented in Scheme 2. The important feature of this diagram is the correlation of $^3D_{\sigma\sigma}$ biradical state of primary products of dissociation with $^3\pi\pi^*$ excited state of alkanone. Despite this assignment is formally correct from the point of view of symmetry of corresponding states, it is not supported by the results of detailed quantum chemical calculations that reveal the presence of considerable energetic barrier separating both states on the hypersurface of the potential energy. These discrepancies led Salem to the reinvestigation of the original assignment[10,11] and the resulting modified diagram is given in Scheme 3. This modification consists in assigning the $^3D_{\sigma\sigma}$



SCHEME 2

biradical state with the high lying $^3\sigma\sigma^*$ state of alkanone whereas the $^3\pi\pi^*$ state of alkanone correlates with some of the excited states of the biradical $^3D_{\sigma\sigma}$ ($^3D^*_{\sigma\sigma}$).



SCHEME 3

The case of photochemical α-cleavage thus represents an example of the reaction, where the standard technique of construction of correlation diagrams based on the assignment of the lowest states of the same symmetry does not lead to the correct results but need to be modified. However, such additional modifications always represent a certain complication since there is usually no *a priori* indication suggesting the necessity of their taking into account. From this aspect it is therefore especially encouraging that the overlap determinant method eliminates the necessity of all such additional modifications and even in conflicting cases directly leads to the correct results. This is due to the fact that the criterion of conservation of electronic configurations[12,13], that represents just the additional condition imposed on the primary symmetry based correlations, is automatically included into the formalism of ODM.

The demonstration of this universality of ODM approach will now be given on the above example of α-splitting reaction. Let us start by the analysis of the correlation of singlet $^1D_{\sigma\sigma}$ biradical state with the ground state of alkanone that requires the nonzero value of the corresponding overlap determinant. Owing to the fact that the reaction $S_0 \rightarrow {}^1D_{\sigma\sigma}$ is represented by splitting just one bond the irreducible core is formed by the electron pair of the dissappearing σ_{CR} bond together with one odd electron with $\alpha(\beta)$ spin on the carbonyl fragment and the second odd electron with $\beta(\alpha)$ spin on the fragment R. Describing these components in a usual way in terms of bonding functions Φ_R, Φ'_P (Eq. (2)) the nonzero value of the corresponding overlap determinant confirms the validity of the original assignment.

$$\begin{aligned}
\Phi_{\mathrm{R}} &= |\sigma_{\mathrm{CR}}\bar{\sigma}_{\mathrm{CR}}| \\
\Phi'_{\mathrm{P}} &= |\sigma'_{\mathrm{C}}\bar{\sigma}'_{\mathrm{R}}|\,, \quad \text{resp.} \quad |\bar{\sigma}'_{\mathrm{C}}\sigma'_{\mathrm{R}}| \\
\sigma_{\mathrm{CR}} &= \chi_{\mathrm{C}} + \chi_{\mathrm{R}} \quad \sigma'_{\mathrm{C}} = \chi'_{\mathrm{C}} \rightarrow \chi_{\mathrm{C}} \\
& \qquad\qquad\qquad\; \sigma'_{\mathrm{R}} = \chi'_{\mathrm{R}} \rightarrow \chi_{\mathrm{R}}
\end{aligned} \tag{2}$$

This result is not surprising since the homolytic splitting of one bond cannot fundamentally alter the nodal structure of corresponding bonding functions and influence thus the allowance of the process.

In the next step let us verify similarly the original assignment correlating the triplet $^3D_{\sigma\sigma}$ state of dissociated reaction products with excited $^3\pi\pi^*$ state of alkanone. Bonding functions describing in this case the structure of the reactant and the product are described by Eq. (*3*).

$$\begin{aligned}
\Phi_{\mathrm{R}} &= |\sigma_{\mathrm{CR}}\bar{\sigma}_{\mathrm{CR}}\pi_{\mathrm{CO}}\pi^*_{\mathrm{CO}}| \\
\Phi'_{\mathrm{P}} &= |\pi'_{\mathrm{CO}}\bar{\pi}'_{\mathrm{CO}}\sigma'_{\mathrm{C}}\sigma'_{\mathrm{R}}|
\end{aligned} \tag{3}$$

Corresponding bonds are expressed in a usual way in terms of atomic orbitals χ and χ' (Eq. (*4*)).

$$\begin{aligned}
\sigma_{\mathrm{CR}} &= \chi^{\sigma}_{\mathrm{C}} + \chi^{\sigma}_{\mathrm{R}} \quad & \pi'_{\mathrm{CO}} &= \chi^{\pi'}_{\mathrm{C}} + \chi^{\pi'}_{\mathrm{O}} \rightarrow \chi^{\pi}_{\mathrm{C}} + \chi^{\pi}_{\mathrm{O}} \\
\pi_{\mathrm{CO}} &= \chi^{\pi}_{\mathrm{C}} + \chi^{\pi}_{\mathrm{O}} \quad & \sigma'_{\mathrm{C}} &= \chi^{\sigma'}_{\mathrm{C}} \rightarrow \chi^{\sigma}_{\mathrm{C}} \\
\pi^*_{\mathrm{CO}} &= \chi^{\pi}_{\mathrm{C}} - \chi^{\pi}_{\mathrm{O}} \quad & \sigma'_{\mathrm{R}} &= \chi^{\sigma'}_{\mathrm{R}} \rightarrow \chi^{\sigma}_{\mathrm{R}}
\end{aligned} \tag{4}$$

Resulting overlap determinant (5) clearly suggests that the transformation of $^3D_{\sigma\sigma}$ and $^3\pi\pi^*$ states is forbidden. Consequently the correlation of these states suggested by the original diagram is wrong.

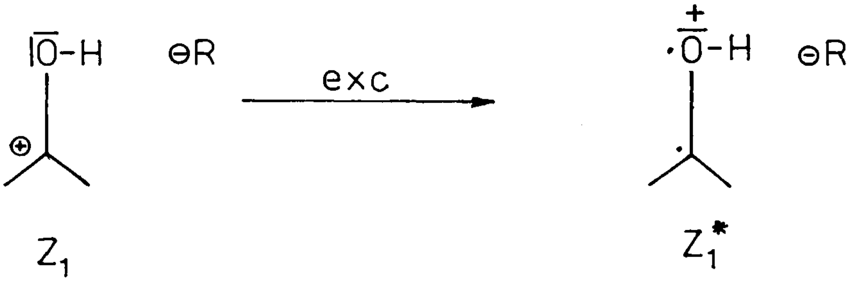
$$D_{^3\pi\pi^* \rightarrow {}^3D_{\sigma\sigma}} = \begin{vmatrix} 0 & 1 & 1 \\ 2 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}_{\alpha} . \, \mathrm{O}_{\beta} = 0 \tag{5}$$

On the other hand the modified Salem diagram suggests the correlation of the biradical $^3D_{\sigma\sigma}$ state with high lying $^3\sigma\sigma^*$ excited state of alkanone. The corresponding overlap determinant can be constructed in a usual way from the bonding functions (*6*).

$$\begin{aligned}
\Phi_{\mathrm{R}} &= |\sigma_{\mathrm{CR}}\sigma^*_{\mathrm{CR}}| \\
\Phi'_{\mathrm{P}} &= |\sigma'_{\mathrm{C}}\sigma'_{\mathrm{R}}|
\end{aligned} \tag{6}$$

Its nonzero value confirms immediately the validity of the modified assignment indicating thus the overlap determinant method automatically leading to the correct diagram without the necessity of introducing any additional modifications and auxiliary concepts.

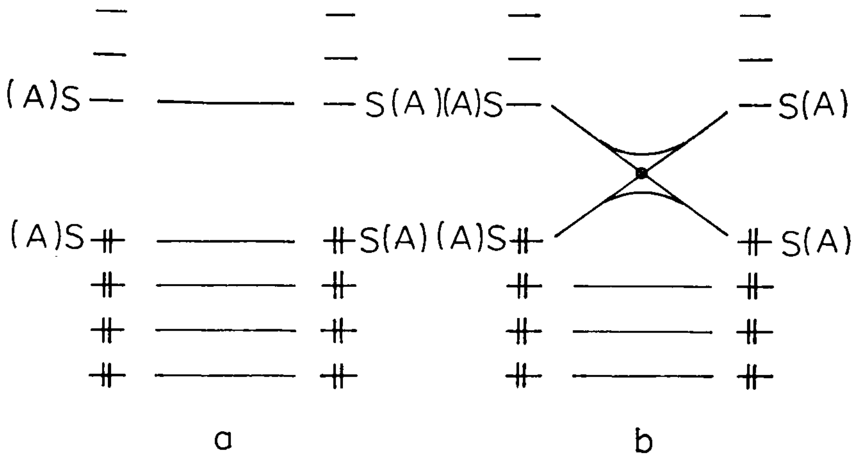
After having discussed the reaction of α-splitting as a typical representative of the feasible forbidden reactions let us return back to the promissed analysis of correlation of $^1\pi\pi^*$ and Z_2 states in H-abstraction reaction. Direct correlation suggested in the original paper[7] was reinvestigated and it was again shown that, it does not satisfy the requirement of the conservation of electronic configurations[10,12,13]. It was therefore modified in such a way that in a new diagram $^1\pi\pi^*$ state correlates with the excited state of the zwitterion $Z_1(Z_1^*)$ (Scheme 4) whereas the Z_2 state correlates with the biexcited $(n\pi^*)^2$ state. For the sake of brevity we will not repeat the whole analysis but we restrict ourselves only to the presentation of bonding functions describing the structure of the corresponding states (Eq. (7)).



SCHEME 4

$$
\begin{aligned}
\Phi_{^1\pi\pi^*} &= \left|n\bar{n}\sigma_{\mathrm{RH}}\bar{\sigma}_{\mathrm{RH}}\pi_{\mathrm{CO}}\bar{\pi}^*_{\mathrm{CO}}\right| \\
\Phi_{\mathrm{Z}_2} &= \left|\sigma_{\mathrm{OH}}\bar{\sigma}_{\mathrm{OH}}\chi^{\pi}_{\mathrm{C}}\bar{\chi}^{\pi}_{\mathrm{C}}\chi^{\pi}_{\mathrm{O}}\bar{\chi}^{\pi}_{\mathrm{O}}\right| \\
\Phi_{\mathrm{Z}_1^*} &= \left|\sigma_{\mathrm{OH}}\bar{\sigma}_{\mathrm{OH}}\sigma_{\mathrm{R}}\bar{\sigma}_{\mathrm{R}}\chi_{\mathrm{O}}\bar{\chi}_{\mathrm{C}}\right| \\
\Phi_{(n\pi^*)^2} &= \left|\sigma_{\mathrm{RH}}\bar{\sigma}_{\mathrm{RH}}\pi_{\mathrm{CO}}\bar{\pi}_{\mathrm{CO}}\pi^*_{\mathrm{CO}}\bar{\pi}^*_{\mathrm{CO}}\right|
\end{aligned}
\qquad (7)
$$

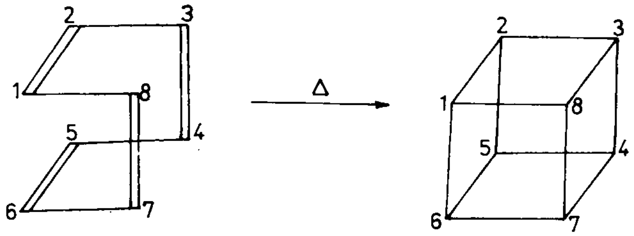
The overlap determinants constructed from these functions confirm again the assignment of the modified diagram demonstrating thus that the overlap determinant method allows a simple and unequivocal construction of the correlation diagrams even in cases where the existing procedures have to be modified by introducing the auxiliary concept of feasible forbidden reactions and/or natural MO correlations[14]. The fact that such modifications were originally proposed for photochemical reactions does not mean, however, that the underlying concepts are inherently restricted to photochemistry. There is also a number of examples, where the similar complications are encountered even for normal ground state reactions. As an example one can mention *e.g.* the concerted cyclization of cyclooctatetraene to cubane. This reaction is interesting by that the symmetry based classical technique of the con-



SCHEME 5

struction of correlation diagrams leads to two alternative assignments schematically depicted in Scheme 5. As it follows from the detailed analysis by Hoffmann the choice between these two alternatives has to take into consideration some additional information about the variation of the orbital energies in the course of the reaction. In our case such a criterion prefers the diagram b that thus represents a typical example of the so-called natural correlation diagram. Its naturality consists in that it takes into consideration what Salem calls the "memory" of molecular orbitals, *i.e.* their ability to select from a number of possible assignments the correct, "natural", one reflecting the requirement of similarity of the nodal structure. The automatic inclusion of this requirement into the formalism of overlap determinant method will be demonstrated on the above example of cyclooctatetraene to cubane transformation.

For the simplicity let us restrict ourselves to the reaction in the ground state only. The irreducible core corresponding to this transformation is given, as it follows from the Scheme 6, by the set of bonds described by Eq. (*8*).



SCHEME 6

$$\begin{aligned} \pi_{12} &= \chi_1 + \chi_2 & \sigma'_{16} &= \chi'_1 + \chi'_6 \\ \pi_{34} &= \chi_3 + \chi_4 & \sigma'_{25} &= \chi'_2 + \chi'_5 \\ \pi_{56} &= \chi_5 + \chi_6 & \sigma'_{38} &= \chi'_3 + \chi'_8 \\ \pi_{78} &= \chi_7 + \chi_8 & \sigma'_{47} &= \chi'_4 + \chi'_7 \end{aligned} \tag{8}$$

Taking into account that the requirement of "concertedness" of the cyclization leads to the assigning tables in the form of simple identity, the primes denoting the bonds in the product can be simply omitted in calculating the overlap determinant. Resulting determinant is given by Eq. (*9*) and its zero value immediately confirms the forbidden nature of the transformation.

$$D = \begin{vmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \end{vmatrix}^2 = 0 \tag{9}$$

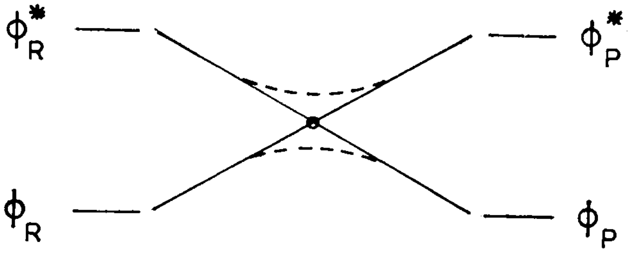
If, on the other hand, one wants to find a structure into which the ground state of cyclooctatetraene is converted during the concerted cyclization, the criterion of overlap determinant suggests that it should be described by the "excited" bonding function (*10*) in which two of the initial bonds are replaced by the virtual ones.

$$\Phi_{\mathrm{P}}^{*\prime} = \left|\sigma_{16}\bar{\sigma}_{16}\sigma^*_{25}\bar{\sigma}^*_{25}\sigma_{38}\bar{\sigma}_{38}\sigma^*_{47}\bar{\sigma}^*_{47}\right| \tag{10}$$

Similarly the ground state of the product correlates with the specifically excited bonding function of the cyclooctatetraene described by the bonding function (*11*)

$$\Phi_{\mathrm{R}}^{*} = \left|\pi_{12}\bar{\pi}_{12}\pi_{34}\bar{\pi}_{34}\pi^*_{56}\bar{\pi}^*_{56}\pi^*_{78}\bar{\pi}^*_{78}\right| . \tag{11}$$

Resulting assignment depicted in Scheme 7 allows to rationalize the presence of the energetic barrier responsible for the "forbiddeness" of the ground state reaction



SCHEME 7

in terms of avoided crossing between the hypersurfaces connecting the ground state of the reactant with the excited state of the product and *vice versa*.

All the above examples demonstrate that the overlap determinant method may serve as a useful alternative procedure for the construction of the correlation diagrams. The encouraging feature of such approach lies above all in the complete universality of overlap determinant method, allowing to construct in a unified manner the correlation diagrams of both Woodward–Hoffmann and Salem type and to classify thus systematically all types of chemical reactions.

REFERENCES

1. Longuet-Higgins H. C., Abrahamson E. W.: J. Amer. Chem. Soc. *87*, 2045 (1965).
2. Woodward R. B., Hoffmann R.: Angew. Chem. *81*, 797 (1969).
3. Mango F. D., Schachtschneider J. H.: J. Amer. Chem. Soc. *89*, 2484 (1967).
4. Mango F. D.: Advan. Catal. Relat. Subj. *20*, 291 (1969).
5. Michl J.: Fortschr. Chem. Forsch. *46*, 1 (1974).
6. Salem L.: Science *91*, 822 (1976).
7. Dauben W., Salem L., Turro N. J.: Accounts Chem. Res. *8*, 41 (1975).
8. Ponec R.: This Journal *49*, 455 (1984).
9. Ponec R.: This Journal *50*, 559 (1985).
10. Salem L., Grimbert D.: Chem. Phys. Lett. *43*, 435 (1976).
11. Salem L., Leforestier C., Segal G., Wetmore F.: J. Amer. Chem. Soc. *97*, 479 (1975).
12. Yamabe S., Minato T., Osamura Y.: Int. J. Quant. Chem. *18*, 243 (1980).
13. Silver D. M.: J. Amer. Chem. Soc. *96*, 5959 (1974).
14. Bigot B., Devaquet A., Turro N. J.: J. Amer. Chem. Soc. *103*, 6 (1980).

Translated by the author.