

# An analogue of the Woodward–Hoffmann rule in terms of bond orders

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## Abstract

The article contains an application to pericyclic reactions of the non-canonical method of molecular orbitals (MOs) suggested previously [V. Gineityte, *J. Mol. Struct. (Theochem)*, 343 (1995) 183; 487 (1999) 231] and based on obtaining the localized MOs (LMOs) and the respective one-electron density matrix (bond order matrix) directly without any reference to delocalized (canonical) MOs. The thermal electrocyclic closure of polyenes containing  $N$  C=C bonds ( $C_{2N}H_{2N+2}$ ) is modelled by emergence of additional resonance parameters between  $2p_z$  AOs of the terminal carbon atoms  $C_1$  and  $C_{2N}$ . At the early stage of the reaction, alterations in the total energies due to the above-specified perturbation are related to bond orders ( $P_{1,2N}$ ) between the terminal AOs of respective initial (open) polyene chain. As a result, an analogue of the famous Woodward–Hoffmann rule is formulated in terms of alternating signs of bond orders  $P_{1,2N}$  for growing  $N$  values. Moreover, a relation is established between the signs of  $P_{1,2N}$  and those of direct (indirect) interactions of orbitals of terminal C=C bonds by means of orbitals of intervening bonds. For later stages of the same process, the relevant alterations in bond orders themselves are studied, and these also are shown to yield an analogous selection rule. An additional insight is given into the mechanism of the closure process, viz. choice between a cyclic- and Möbius-array-like overlap topology of  $2p_z$  AOs of carbon atoms is shown to be made at the very early stage of the reaction. Inasmuch as bond order matrices are closely related to respective LMOs and thereby belong to the localized way of representing electronic structures (see the above-cited references), the results obtained may be considered as a localized description of pericyclic reactions.

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## 1. Introduction

Numerous pericyclic reactions have been discovered and studied within the last decades including the so-called electrocyclic transformations [1–3]. Definition of these reactions involves an assumption that a ‘concerted reorganization of bonding occurs throughout a cyclic array of continuously bounded atoms’ [1]. In other terms, no local reaction center is supposed to be peculiar to these processes in contrast to other organic reactions. It is no surprise in this connection that the canonical method of delocalized molecular orbitals (the CMO method) proved to be extremely successful in interpretation of pericyclic reactions.

The first accounting for the high stereospecificity of electrocyclic transformations was based on consideration of

symmetry properties of CMOs. In particular, the highest-occupied MO (HOMO) of the acyclic member of the reactant–product pair [4–6] was shown to play the most important role in the thermal electrocyclic closure processes of polyenes. On this basis, the famous selection rule was formulated, and it is known nowadays as the Woodward–Hoffmann rule.

Several extended approaches to interpretation of the same reactions have been developed later including the MO and/or state correlation diagrams on going from reactant through transition state to product [7], the frontier MO (FMO) theory [8] and studies of stability of the supposed transition state by invoking the concept of the Hückel and Möbius aromaticity [9,10]. It is also noteworthy here that all the above-enumerated approaches are directly or indirectly based on consideration of CMOs and their transformations during the process.

It is known, however, that the set of CMOs is not the only possible set of one-electron orbitals of a molecular

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system [11,12]. Moreover, orbitals localized mainly on particular chemical bonds of the given system may be found among alternative (non-canonical) sets of MOs, and these are usually referred to as localized MOs (LMOs). Accordingly, localized approaches present an alternative to the delocalized way of representing electronic structures based on CMOs. Applicability of these approaches to polyenes of a small and medium size is beyond any doubt [13,14].

The most traditional way of obtaining LMOs consists in transforming the set of occupied CMOs using various localization criteria [11,12]. As it turned out later, however, both canonical and non-canonical MOs (NCMOs) may be obtained directly without invoking the alternative set [15–19]. On this basis, an equivalence of the CMO and NCMO methods has been concluded [14]. Moreover, these methods were shown to describe complementary aspects of electronic structures. In this context, a question of particular interest is about applicability of the NCMO method to pericyclic reactions.

The direct way of obtaining LMOs [15–19] is based on the Brillouin theorem, which, in turn, resolves itself into the block-diagonalization problem for the relevant Fockian or Hückel type Hamiltonian matrix. To solve this problem, the so-called non-commutative Rayleigh–Schrödinger perturbation theory (NCRSPT) has been developed [18,19]. An important feature of this approach consists in the relation between the block-diagonalization problem and the direct way of obtaining the respective one-electron density matrix (DM) on the basis of solution of the commutation equation [18]. As a consequence, interrelated power series have been derived for the DM ( $P$ ) and for the relevant LMO representation matrix ( $T$ ) that are expected to converge (or diverge) simultaneously [14,18]. This implies the matrices  $T$  and  $P$  to offer alternative localized representations of electronic structures.

Under these circumstances, adequacy of the one-electron DM (bond order matrix) for interpretation of pericyclic reactions (if established) would imply applicability of the localized approach in general. Moreover, equivalence of the localized and delocalized ways of representing electronic structures [14] would acquire an additional support. Finally, some new aspects of the very reaction mechanism may be expected to follow. It is precisely the exploration of applicability of the bond order matrix to pericyclic reactions that this paper is aimed at.

As an initial step of this work, we will consider the thermal electrocyclic closure of polyenes. We are about to demonstrate that the famous Woodward–Hoffmann rule [1–6] (the reaction is allowed in the disrotatory and conrotatory fashions for systems of  $4n+2$  and  $4n$  electrons, respectively) may be formulated on the basis of bond orders without any reference to canonical MOs. To this end, we will employ the power series for the DM  $P$  resulting from the direct solution of the commutation equation by means of the NCRSPT [18].

Members of the above-mentioned power series have been expressed in terms of principal matrices  $G_{(k)}$  describing the direct (through-space) and indirect (through-bond) interactions of bond orbitals ( $k$  here and below stands for the order parameter). The very concept of direct and indirect interactions has been suggested in Refs. [20–23] and used for interpretation of photoelectron spectra of molecules [20–29] and of localized MOs [15–18,30,31]. Employment of these terms for interpretation of pericyclic reactions is also among the aims of the present study.

In the framework of the Hückel model, the electrocyclic closure of a polyene chain may be modelled by emergence of a new resonance parameter between AOs of the terminal carbon atoms. At the very early stage of the reaction, this additional parameter may be assumed to take a small value vs. those of the initially single (C–C) bonds. Sections 2 and 3 are devoted to investigation of just this case, viz. of alterations in total energies due to the above-specified perturbation of the chain. When the process goes on and the new resonance parameter becomes comparable with those of the C–C bonds, changes in the internal bond orders of the chain also may be revealed. The results of the relevant investigation are overviewed in Section 4.

## 2. Studies of an early stage of the closure process. The expressions for bond orders

Let us start with an open polyene chain ( $C_{2N}H_{2N+2}$ ) containing  $N$  C=C bonds and  $2N$   $\pi$ -electrons. Let the system of coordinates to be chosen so that the principal plane of the molecule coincides with the  $xy$  plane (Fig. 1). The carbon atoms of this chain will be then represented by  $2p_z$  AOs  $\chi_1, \chi_2, \dots, \chi_{2N}$  that are supposed to be characterized by uniform Coulomb parameters  $\alpha$ . Resonance parameters between pairs of neighboring AOs ( $\chi_r, \chi_{r+1}$ ) also will be assumed to take uniform values  $\beta$  for simplicity [14]. For other pairs of AOs, the resonance parameters are supposed to take zero values.

Let us assume now that an additional local perturbation represented by the resonance parameter  $\gamma_{1,2N}$  between the terminal AOs  $\chi_1$  and  $\chi_{2N}$  arises in our chain due to its closure. Inasmuch as bond orders  $P_{1,2N}$  between these AOs take non-zero values in the initial (open) polyene chain [14],

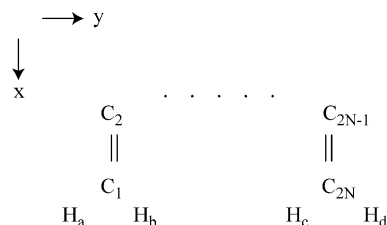


Fig. 1. The initial arrangement of the terminal bonds ( $C_1=C_2$  and  $C_{2N-1}=C_{2N}$ ) of the polyene chain  $C_{2N}H_{2N+2}$  with respect to the system of coordinates. The labels attributed to the terminal hydrogen atoms serve to display the same molecule in the plane  $xy$  in Fig. 2.

the relevant alterations in total energies coincide with the first order corrections defined as follows [32–34]

$$\Delta E \approx E_{(1)} = 2P_{1,2N}\gamma_{1,2N}. \quad (1)$$

Let the energy reference point to be defined by an assumption that  $\alpha=0$ . Moreover, the equality  $\beta=1$  will be accepted and this implies our energy unit to be negative. We may then expect that positive corrections  $E_{(1)}$  correspond to allowed reactions, whereas negative ones refer to forbidden processes.

Let us consider now the closure process in more detail (Fig. 2). The negative lower lobes of the  $2p_z$  AOs  $\chi_1$  and  $\chi_{2N}$  will overlap one with another most significantly during a disrotatory reaction (Fig. 2a). Consequently, a disrotatory process is accompanied by formation of a positive overlap integral  $S_{1,2N}$  between AOs  $\chi_1$  and  $\chi_{2N}$  and thereby of a positive resonance parameter ( $\gamma_{1,2N}^{(dis)} > 0$ ). Again, a conrotatory way of reaction gives rise to the primary overlap of lobes of AOs  $\chi_1$  and  $\chi_{2N}$  of different signs and thereby to a negative value of the same parameter ( $\gamma_{1,2N}^{(con)} < 0$ ). It may be expected, therefore, that allowed thermal reactions proceed in a disrotatory fashion if  $P_{1,2N} > 0$ , whilst the same processes chose a conrotatory way if  $P_{1,2N} < 0$ , where the  $P_{1,2N}$  evidently refers to the acyclic hydrocarbon. Hence, it is the sign of the bond order between the terminal AOs of the open polyene that determines the predominant way of its subsequent closure process. This implies that establishing the dependence between the sign of the bond order  $P_{1,2N}$  and the total number of electrons in the chain is the principal aim of our study. To this end, we are about to derive and analyze the algebraic expressions for  $P_{1,2N}$  using the above-discussed power series for the bond order matrix [18,35].

Members of this series have been originally represented [18] in the basis of bonding and antibonding orbitals of the initially double (C=C) bonds that were referred to as bond orbitals (BOs). The latter, in turn, have been defined as normalized sums and differences of pairs of  $2p_z$  AOs involved within separate C=C bonds. For example, BOs of the first and of the last C=C bond

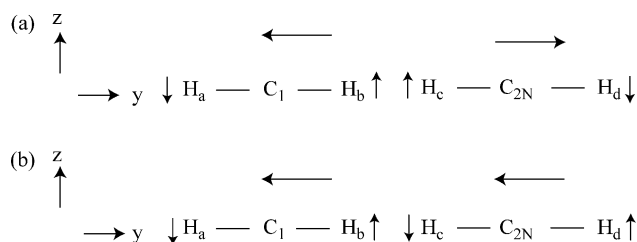


Fig. 2. Schemes representing the disrotatory (a) and the conrotatory (b) closures of the chain from the front of the molecule.

take the form

$$\begin{aligned} \varphi_{(+i)}\varphi_{(-j)} &= \frac{1}{\sqrt{2}}(\chi_1 \pm \chi_2); \\ \varphi_{(+iN)}\varphi_{(-jN)} &= \frac{1}{\sqrt{2}}(\chi_{2N-1} \pm \chi_{2N}), \end{aligned} \quad (2)$$

where the subscripts (+) and (−) here and below stand for the bonding BOs (BBOs) and antibonding BOs (ABOs), respectively. The upper and lower signs of the right-hand sides of these expressions also correspondingly refer to BBOs and ABOs. Let the notation  $\tilde{P}$  stand for the bond order matrix of polyenes in the basis of BOs.

To derive the expression for  $P_{1,2N}$ , however, an alternative representation of the DM in the basis of  $2p_z$  AOs is evidently required. The latter is easily obtainable by transforming the original matrix  $\tilde{P}$  into the basis of AOs. The relevant unitary transformation matrix may be constructed using the definition of BOs of Eq. (2). The final expression for the bond order  $P_{1,2N}$  takes the form

$$P_{1,2N} = \frac{1}{2}(\tilde{P}_{(+i),(+j)N} - \tilde{P}_{(-i),(-j)N} + \tilde{P}_{(+i)N,(-j)} - \tilde{P}_{(+i),(-j)N}). \quad (3)$$

The right-hand side of Eq. (3) contains elements of the DM  $\tilde{P}$  in the basis of BOs, the latter being indicated by subscripts (+) $i$  and (−) $j$ . Expressions for these elements may be taken from Refs. [18,35] and are discussed below.

Let us start with partition of the relevant initial Hamiltonian matrix  $\tilde{H}$  of Refs. [18,35]. The zero order term  $\tilde{H}_{(0)}$  was assumed to coincide with a diagonal matrix containing one-electron energies of BOs, whereas the first order matrix  $\tilde{H}_{(1)}$  involved resonance parameters between BOs. An assumption about relatively small values of the latter vs. the energy differences between BBOs and ABOs formed the basis of expressions for elements  $\tilde{P}_{ij}$  as sums of corrections  $\tilde{P}_{ij}^{(k)}$  of various orders ( $k$ ). Convergence of this power series for open polyene chains of small and medium size has been verified in Ref. [14].

Given that the subscripts  $i$  and  $j$  correspond to a BBO ( $\varphi_{(+i)}$ ) and to an ABO ( $\varphi_{(-j)}$ ), respectively, as it is the case with last two elements of the right-hand side of Eq. (3), the corrections  $\tilde{P}_{(+i),(-j)}^{(k)}$  ( $k=1,2,3,\dots$ ) take the form

$$\tilde{P}_{(+i),(-j)}^{(k)} = -2G_{(k)ij}, \quad (4)$$

where  $G_{(k)ij}$  are elements of the principal matrices  $G_{(k)}$  introduced previously [18] and determining various types of direct and indirect interactions between orbitals  $\varphi_{(+i)}$  and  $\varphi_{(-j)}$ .

The zero order term  $\tilde{P}_{(+i),(-j)}^{(0)}$  of Eq. (4) takes a zero value. The first order element  $G_{(1)ij}$  determining the correction  $\tilde{P}_{(+i),(-j)}^{(1)}$  has been expressed as follows

$$G_{(1)ij} = -\frac{\langle \varphi_{(+i)} | \hat{H} | \varphi_{(-j)} \rangle}{E_{(+i)} - E_{(-j)}} \quad (5)$$

and described the direct (through-space) interaction between orbitals  $\varphi_{(+i)}$  and  $\varphi_{(-j)}$ . The numerator of the right-hand side of Eq. (5) contains the Hückel type Hamiltonian matrix element (resonance parameter) between basis orbitals indicated within the bra- and ket-vectors, and the denominator involves the relevant difference in one-electron energies.

Similarly, the second order element  $G_{(2)ij}$  takes the form

$$G_{(2)ij} = \frac{1}{E_{(+i)} - E_{(-j)}} \times \left\{ \sum_m^{\text{BBOs}} \frac{S_{im}R_{mj}}{E_{(+m)} - E_{(-j)}} - \sum_n^{\text{ABOs}} \frac{R_{in}Q_{nj}}{E_{(+i)} - E_{(-n)}} \right\}, \quad (6)$$

where the meanings of designations coincide with those of Eq. (5), and

$$\begin{aligned} S_{im} &= \langle \varphi_{(+i)} | \hat{H} | \varphi_{(+m)} \rangle, \\ R_{mj} &= \langle \varphi_{(+m)} | \hat{H} | \varphi_{(-j)} \rangle, \\ Q_{nj} &= \langle \varphi_{(-n)} | \hat{H} | \varphi_{(-j)} \rangle. \end{aligned} \quad (7)$$

This element describes the indirect interaction between the same orbitals by means of a single mediator, and both the BBOs ( $\varphi_{(+m)}$ ) and ABOs ( $\varphi_{(-n)}$ ) are able to play this role. To be an efficient mediator, however, the orbital under consideration should overlap with both  $\varphi_{(+i)}$  and  $\varphi_{(-j)}$ . Hence, orbitals situated in between the indirectly interacting orbitals meet this condition best of all.

Finally, the element  $G_{(3)ij}$  describes the indirect interaction of BOs  $\varphi_{(+i)}$  and  $\varphi_{(-j)}$  by means of two mediators. The expression for this element takes the form [35]

$$\begin{aligned} G_{(3)ij} &= \frac{-1}{E_{(+i)} - E_{(-j)}} \left\{ \sum_n^{\text{BBOs}} \sum_m^{\text{BBOs}} \frac{S_{in}S_{nm}R_{mj}}{(E_{(+n)} - E_{(-j)})(E_{(+m)} - E_{(-j)})} - \sum_n^{\text{BBOs}} \sum_r^{\text{ABOs}} \left[ \frac{S_{in}R_{nr}Q_{rj}}{(E_{(+n)} - E_{(-j)})(E_{(+n)} - E_{(-r)})} \right. \right. \\ &+ \left. \frac{S_{in}R_{nr}Q_{rj}}{(E_{(+i)} - E_{(-r)})(E_{(+n)} - E_{(-r)})} + \frac{R_{ir}R_{rn}^+R_{nj}}{(E_{(+n)} - E_{(-r)})(E_{(+r)} - E_{(-j)})} + \frac{R_{ir}R_{rn}^+R_{nj}}{(E_{(+i)} - E_{(-r)})(E_{(+n)} - E_{(-r)})} \right] \\ &+ \left. \sum_p^{\text{ABOs}} \sum_r^{\text{ABOs}} \frac{R_{ir}Q_{rp}Q_{pj}}{(E_{(+i)} - E_{(-p)})(E_{(+i)} - E_{(-r)})} \right\}. \end{aligned} \quad (8)$$

Pairs of mutually overlapping orbitals situated in between the BOs  $\varphi_{(+i)}$  and  $\varphi_{(-j)}$  are the most efficient mediators of this indirect interaction.

Let us turn again to Eq. (3) and consider the remaining elements  $\tilde{P}_{ij}$ . If both subscripts  $i$  and  $j$  refer to BBOs, we obtain

$$\begin{aligned} \tilde{P}_{(+i),(+j)}^{(0)} &= 2\delta_{ij}; \quad \tilde{P}_{(+i),(+j)}^{(1)} = 0; \\ \tilde{P}_{(+i),(+j)}^{(2)} &= -2 \sum_r^{\text{ABOs}} G_{(1)ir} G_{(1)rj}^+; \\ \tilde{P}_{(+i),(+j)}^{(3)} &= -2 \sum_r^{\text{ABOs}} (G_{(1)ir} G_{(2)rj}^+ + G_{(2)ir} G_{(1)rj}^+), \end{aligned} \quad (9)$$

where the superscripts of the left-hand sides indicate the orders of respective corrections, whilst the superscripts + of the right-hand sides denote elements of the Hermitian-conjugate matrices  $G_{(k)}^+$ .

Finally, for both  $i$  and  $j$  corresponding to ABOs, the relevant corrections are

$$\begin{aligned} \tilde{P}_{(-i),(-j)}^{(0)} &= \tilde{P}_{(-i),(-j)}^{(1)} = 0; \\ \tilde{P}_{(-i),(-j)}^{(2)} &= 2 \sum_m^{\text{BBOs}} G_{(1)im}^+ G_{(1)mj}; \\ \tilde{P}_{(-i),(-j)}^{(3)} &= 2 \sum_m^{\text{BBOs}} (G_{(1)im}^+ G_{(2)mj} + G_{(2)im}^+ G_{(1)mj}). \end{aligned} \quad (10)$$

Before finishing this section, let us note that the right-hand sides of Eqs. (9) and (10) also may be interpreted as indirect interactions between respective pairs of BOs, i.e. between  $\varphi_{(+i)}$  and  $\varphi_{(+j)}$ , and between  $\varphi_{(-i)}$  and  $\varphi_{(-j)}$ , respectively.

### 3. Alternation of bond orders between the terminal AOs of polyene with increasing number of C=C bonds

In this section, we are about to study the dependence between the sign of the bond order  $P_{1,2N}$  and the total number of C=C bonds ( $N$ ) and thereby of electrons in the chain. To this end, Eqs. (3)–(10) will be used.

It is known that open polyenes are among the so-called alternant hydrocarbons that are characterized by specific peculiarities of Hamiltonian matrices and thereby of related terms. In particular, the principal matrices  $G_{(k)}$

of these molecules were shown to be skew-symmetric (skew-Hermitian) matrices [14], i.e.  $G_{(k)}^+ = -G_{(k)}$ . For separate elements of these matrices, we accordingly obtain

$$G_{(k)ij}^+ = -G_{(k)ij} = G_{(k)ji}. \quad (11)$$

This relation implies coincidence of absolute values and opposite signs for interactions of any order ( $k$ ) between definite pairs of orbitals of the  $i$ th and  $j$ th bonds, namely between orbitals  $\varphi_{(+i)}$  and  $\varphi_{(-j)}$  and between  $\varphi_{(+j)}$  and  $\varphi_{(-i)}$ .

Using Eqs. (4) and (11) we then obtain

$$\tilde{P}_{(+N,(-)1} = -\tilde{P}_{(+1,(-)N}. \quad (12)$$

Similarly, Eqs. (9)–(11) yield the relation

$$\tilde{P}_{(+1,(+N)} = -\tilde{P}_{(-1,(-)N}. \quad (13)$$

As a result, Eq. (3) may be simplified as follows

$$P_{1,2N} = \tilde{P}_{(+1,(+N)} - \tilde{P}_{(+1,(-)N}. \quad (14)$$

Let us turn now to particular polyenes and start with the butadiene molecule ( $N=2$ ). The structure of respective BOs follows from Eq. (2). It is evident that orbitals of C=C bonds interact directly in this case and thereby first order elements  $G_{(1)12}$  and  $G_{(1)21}$  take non-zero values. This, in turn, implies that the first order correction  $P_{1,2N}^{(1)}$  defined by Eq. (4) yields the principal contribution to the bond order  $P_{1,4}$ . Using Eqs. (2), (5), (7) and (14) we then obtain

$$R_{12} = \frac{1}{2}, \quad G_{(1)12} = -\frac{1}{4}, \quad (15)$$

$$P_{1,4} \approx P_{1,4}^{(1)} = -\tilde{P}_{(+1,(-)2}^{(1)} = 2G_{(1)12} = -\frac{1}{2} < 0.$$

It is seen that a negative bond order between AOs  $\chi_1$  and  $\chi_4$  of butadiene arises owing to the negative value of the direct interaction  $G_{(1)12}$ .

For the hexatriene molecule ( $N=3$ ), orbitals of terminal bonds interact indirectly by means of BOs of the mediating bond ( $C_3=C_4$ ). Consequently, second order corrections yield the most important contributions in this case. Thus, from Eq. (9) we obtain

$$\tilde{P}_{(+1,(+3)} \approx \tilde{P}_{(+1,(+3)}^{(2)} = -2G_{(1)12}G_{(1)23}^+ = \frac{1}{8}. \quad (16)$$

Again, orbitals  $\varphi_{(+2)}$  and  $\varphi_{(-2)}$  play the role of mediators in the indirect interaction  $G_{(2)13}$  and

$$\tilde{P}_{(+1,(-)3} \approx \tilde{P}_{(+1,(-)3)}^{(2)} = -2G_{(2)13} = -\frac{1}{4}. \quad (17)$$

Substituting Eqs. (16) and (17) into Eq. (14) yields the following final result

$$P_{1,6} \approx \tilde{P}_{1,6}^{(2)} = \frac{3}{8} > 0 \quad (18)$$

indicating a positive sign of the bond order  $P_{1,6}$  between the terminal AOs of the hexatriene. The positive indirect interaction  $G_{(2)13}$  yields the most significant contribution to the above-mentioned result.

Finally, third order indirect interactions contribute most substantially to the bond order  $P_{1,8}$  between AOs  $\chi_1$  and  $\chi_8$  of the octatriene molecule ( $N=4$ ). The first increment of this correction ( $\tilde{P}_{(+1,(+4)}^{(3)}$ ) follows from the last relation of Eq. (9). Inasmuch as  $G_{(1)1r} \neq 0$  for  $r=(-)2$  and  $G_{(1)r4}^+ = G_{(1)4r} \neq 0$  for  $r=(-)3$ , we obtain

$$\tilde{P}_{(+1,(+4)}^{(3)} = -2(G_{(1)12}G_{(2)42} + G_{(2)13}G_{(1)43}), \quad (19)$$

where

$$G_{(1)12} = -\frac{1}{4}, \quad G_{(1)43} = \frac{1}{4}, \quad (20)$$

$$G_{(2)42} = -\frac{1}{8}, \quad G_{(2)13} = \frac{1}{8}.$$

Substituting Eq. (20) into Eq. (19) yields

$$\tilde{P}_{(+1,(+4)} \approx \tilde{P}_{(+1,(+4)}^{(3)} = -\frac{1}{8} < 0. \quad (21)$$

Let us turn now to the second increment of the same bond order, viz. to  $\tilde{P}_{(+1,(-)4}^{(3)}$  defined by Eq. (4). Four pairs of orbitals of intervening bonds, viz.  $(\varphi_{(+2)}, \varphi_{(+3)})$ ,  $(\varphi_{(+2)}, \varphi_{(-3)})$ ,  $(\varphi_{(-2)}, \varphi_{(+3)})$  and  $(\varphi_{(-2)}, \varphi_{(-3)})$ , are able to play the role of mediators in the third order indirect interactions  $G_{(3)14}$  determining the increment  $\tilde{P}_{(+1,(-)4}^{(3)}$ . As a result, the following expression may be derived from Eq. (8)

$$G_{(3)14} = -\frac{1}{8}[S_{12}S_{23}R_{34} - 2S_{12}R_{23}Q_{34} - 2R_{12}R_{23}^+R_{34} + R_{12}Q_{23}Q_{34}]. \quad (22)$$

After substituting the appropriate values of resonance parameters we obtain that

$$G_{(3)14} = -\frac{3}{32} < 0, \quad \tilde{P}_{(+1,(-)4} \approx \tilde{P}_{(+1,(-)4}^{(3)} = \frac{3}{16} > 0 \quad (23)$$

and

$$P_{1,8} \approx P_{1,8}^{(3)} = -\frac{5}{16} < 0. \quad (24)$$

Hence, the bond order  $P_{1,8}$  between the terminal AOs of octatriene proves to be negative as it was the case with butadiene (see Eq. (15)). This result may be traced back to the negative value of the indirect interaction  $G_{(3)14}$  seen from Eq. (23).

It may be concluded, therefore, that the signs of bond orders  $P_{1,2N}$  between terminal orbitals of open polyene chains alternate with increasing total number of C=C bonds ( $N$ ). A similar conclusion follows also from comparison of the relevant results of numerical calculations [14]. In contrast to the latter, however, the above-outlined way of derivation of bond orders yields an additional relation between the sign of the bond order  $P_{1,2N}$  and that of the respective direct or indirect interaction of orbitals of terminal bonds, namely both signs prove to alternate simultaneously with growing total number of C=C bonds. Furthermore, negative bond orders  $P_{1,2N}$  and thereby a conrotatory closure of the chain is predicted for even  $N$  values, whereas positive signs of  $P_{1,2N}$  and thereby a disrotatory process follows for odd  $N$  values. Inasmuch as  $4n$  and  $4n+2$  electrons, respectively, correspond to these cases, the above-established result coincides with the Woodward–Hoffmann rule [1–6]. Thus, it may be accordingly regarded as the analogue of this rule in terms of bond orders.



#### 4. Exploration of a later stage of closure. Alterations in the internal bond orders

Bond orders  $P_{1,2N}$  between terminal AOs  $\chi_1$  and  $\chi_{2N}$  of the initial (open) polyene chain determine the predominant way of the closure process at the very early stage of the reaction as demonstrated in Sections 2 and 3. When the process goes on, however, certain alterations in bond orders themselves may be expected that refer both to  $P_{1,2N}$  and to the internal bond orders. In this section, we are about to explore the nature of these alterations for allowed and forbidden processes. To this end, the new resonance parameter  $\gamma_{1,2N}$  will be included into the first order Hamiltonian matrix along with resonance parameters referring to the initially single (C–C) bonds. The notation  $\gamma$  will be used below instead of  $\gamma_{1,2N}$  for simplicity.

Let us start with the butadiene molecule ( $N=2$ ). Emergence of the new resonance parameter  $\gamma$  between AOs  $\chi_1$  and  $\chi_4$  yields the following relations

$$\begin{aligned} R_{12}^{(\gamma)} &= \frac{1}{2} - \frac{\gamma}{2}, & G_{(1)12}^{(\gamma)} &= -G_{(1)21}^{(\gamma)} \\ &= -\frac{1}{4} + \frac{\gamma}{4}, & P_{1,4}^{(\gamma)} &= -\frac{1}{2} + \frac{\gamma}{2} \end{aligned} \quad (25)$$

instead of Eq. (15), where the superscript ( $\gamma$ ) is used here and below for respective modified characteristics of the chain. Comparison of Eqs. (15) and (25) shows that an additional increase of the absolute value of  $P_{1,4}$  is observed for negative  $\gamma$  values, but not for positive ones.

Let us consider now the alteration in the internal bond order  $P_{23}$  of the initially single bond of butadiene (C<sub>2</sub>–C<sub>3</sub>). The relevant definition takes the form

$$P_{23} = \frac{1}{2} (\tilde{P}_{(+1),(+2)} - \tilde{P}_{(-1),(-2)} + \tilde{P}_{(+1),(-2)} - \tilde{P}_{(+2),(-1)}) \quad (26)$$

and resembles Eq. (3). The expression for  $P_{23}^{(\gamma)}$  also may be obtained similarly and takes the form

$$P_{23}^{(\gamma)} = \frac{1}{2} - \frac{\gamma}{2}, \quad (27)$$

where the first increment of the right-hand side (i.e.  $\frac{1}{2}$ ) refers to the open butadiene chain. It is seen that an increase of the bond order of the initially single bond (C<sub>2</sub>–C<sub>3</sub>) results for negative  $\gamma$  values.

The remaining bond order of butadiene corresponding to an initially double bond may be expressed as follows

$$P_{12} = \frac{1}{2} (\tilde{P}_{(+1),(+1)} - \tilde{P}_{(-1),(-1)}) \quad (28)$$

and contains occupation numbers of BOs of the bond under consideration. First order corrections to populations of BOs were shown to take zero values [18]. Consideration of the second order increments yields the following expression for

the modified bond order  $P_{12}^{(\gamma)}$

$$P_{12}^{(\gamma)} = 1 - [(G_{(1)12}^{(\gamma)})^2 + (G_{(1)21}^{(\gamma)})^2] = 1 - \frac{1}{8}(1 - \gamma)^2, \quad (29)$$

where the last relation is obtained after substituting the modified matrix element  $G_{(1)12}^{(\gamma)}$  of Eq. (25). From Eq. (29) it follows that the bond order of the initially double bond becomes reduced more substantially if a negative  $\gamma$  value is assumed.

Hence, redistributions of bond orders of the appropriate nature are ensured if a negative  $\gamma$  value and thereby a conrotatory way of closure of the butadiene chain is chosen.

Other polyenes also may be studied similarly. Thus, emergence of the new resonance parameter  $\gamma = \gamma_{1,6}$  between AOs  $\chi_1$  and  $\chi_6$  of the hexatriene molecule gives rise to first order (direct) interactions between BOs of terminal bonds (C<sub>1</sub>=C<sub>2</sub> and C<sub>5</sub>=C<sub>6</sub>) and thereby to a definite alteration of the bond order  $P_{1,6}$ , the initial value of which is shown in Eq. (18). We obtain

$$G_{(1)13}^{(\gamma)} = -G_{(1)31}^{(\gamma)} = \frac{\gamma}{4}, \quad P_{1,6}^{(\gamma)} = \frac{3}{8} + \frac{\gamma}{2}. \quad (30)$$

Thus, the positive bond order of Eq. (18) becomes additionally increased if a positive parameter  $\gamma$  is introduced.

So far as bond orders of the initially single bonds of hexatriene are concerned, a  $\gamma$ -independent first order correction equal to  $\frac{1}{2}$  results from Eq. (26). This implies that higher order corrections should be considered by invoking Eqs. (6), (9) and (10). For separate increments of the right-hand side of Eq. (26), we then obtain

$$\tilde{P}_{(+1),(+2)}^{(\gamma)} = -\tilde{P}_{(-1),(-2)}^{(\gamma)} = \frac{\gamma}{8}, \quad \tilde{P}_{(+1),(-2)}^{(\gamma)} = -\tilde{P}_{(+2),(-1)}^{(\gamma)} = \frac{\gamma}{2}, \quad (31)$$

where the relations shown in Eqs. (12) and (13) also are taken into account. Substituting Eq. (31) into Eq. (26) yields the following final result

$$P_{23}^{(\gamma)} = P_{45}^{(\gamma)} = \frac{1}{2} + \frac{5\gamma}{8}. \quad (32)$$

It is seen that a positive parameter  $\gamma$  ensures an increase of bond orders of initially single bonds of hexatriene.

The bond order  $P_{12}$  of the C<sub>1</sub>=C<sub>2</sub> bond of hexatriene may be found on the basis of Eq. (28), whereas that of the C<sub>3</sub>=C<sub>4</sub> bond is defined as follows

$$P_{34} = \frac{1}{2} (\tilde{P}_{(+2),(+2)} - \tilde{P}_{(-2),(-2)}). \quad (33)$$

Dependence of these bond orders upon the sign of the new parameter  $\gamma$  arises within the third order terms only. To reveal this dependence, the expressions for  $\tilde{P}_{(+i),(+j)}^{(3)}$  and for  $\tilde{P}_{(-i),(-j)}^{(3)}$  shown in Eqs. (9) and (10) should be used. The final result of such a consideration is as follows

$$P_{12}^{(\gamma)} = 1 - \frac{1}{8} - \frac{\gamma^2}{8} - \frac{3\gamma}{4}, \quad P_{34}^{(\gamma)} = 1 - \frac{1}{4} - \frac{3\gamma}{4} \quad (34)$$

and indicates more substantial reductions of bond orders of the initially double bonds for positive  $\gamma$  values. Thus, redistributions of bond orders of hexatriene comply with our expectations for positive  $\gamma$  values and thereby under an assumption of disrotatory way of closure of the chain.

It is seen, therefore, that alterations in bond orders during the closure process yield predictions of the predominant ways of reaction that coincide with those following from consideration of bond orders between the terminal AOs of the initial (open) polyene chain. Hence, the Woodward–Hoffmann rule based on studies of the acyclic members of the reagent–product pairs acquire an additional support.

## 5. Conclusions

The principal result of the above study consists in formulating the analogue of the Woodward–Hoffmann rule for electrocyclic transformations on the basis of the bond order matrix, the latter being obtainable directly without invoking the canonical (delocalized) MOs.

The main points underlying this rule are as follows:

1. Positive and negative overlap integrals  $S_{1,2N}$  are supposed to arise between the terminal  $2p_z$  AOs of polyenes at the very outset of a disrotatory and conrotatory closure processes, respectively.
2. Choice of the allowed way of the closure process is determined by the sign of the bond order ( $P_{1,2N}$ ) between terminal AOs  $\chi_1$  and  $\chi_{2N}$  of the initial (open) polyene chain, viz. positive (negative) bond orders predetermine disrotatory (conrotatory) way of closure.
3. The above-mentioned sign of  $P_{1,2N}$  alternates with increasing total number of C=C bonds ( $N$ ), namely negative (positive) bond orders correspond to even (odd) numbers of C=C bonds ( $N$ ).
4. The bond orders  $P_{1,2N}$ , in turn, depend on certain matrix elements describing the interactions between orbitals of the terminal C=C bonds either directly (cf. the case  $N=2$  referring to the butadiene molecule) or indirectly by means of orbitals of intervening bonds. Accordingly, alternation of signs of  $P_{1,2N}$  is determined by an analogous behaviour of the above-specified interaction with growing number of intervening bonds.
5. Selection rules based on studies of an initial (open) chain are supported by investigations of subsequent alterations in bond orders during later stages of the closure process.
6. Redistributions of bond orders of the appropriate nature are ensured under an assumption about conservation of signs of resonance parameters  $\gamma_{1,2N}$  and of overlap integrals  $S_{1,2N}$  when passing from the very early stage of the process to its later stages.

Implications of the results obtained for understanding the mechanism of the closure process also deserve mentioning here:

1. In accordance with the above-established signs of additional overlap integrals  $S_{1,2N}$  between the terminal AOs of polyenes, formation of a usual cyclic array of  $2p_z$  AOs and of a Möbius array may be expected to take place at the very early stage of the closure process for the cases of odd and even total numbers of C=C bonds, respectively.
2. Conservation of signs of overlap integrals  $S_{1,2N}$  when passing to later stages of the reaction along with the concept of the Hückel and Möbius aromaticity of corresponding transition structures for odd and even  $N$  values [9,10] indicate that the cyclic- and the Möbius-array-like overlap topologies, respectively, are peculiar to closure processes within wide ranges of reaction coordinates.
3. Choice between the cyclic- and the Möbius-array-like overlap topology of the closure process is determined by the nature of the (direct or indirect) interaction of orbitals of terminal C=C bonds by means of orbitals of intervening bonds, the latter being actually conditioned by the total number of C=C bonds in the chain.

Generally, the following points proved to be supported by the results of the above study:

- (1) Adequacy of the non-canonical method of MOs and thereby of the localized way of representing electronic structures for interpretation of pericyclic reactions;
- (2) Equivalence of the localized and delocalized approaches to investigate electronic structures in general [14] and the pericyclic reactions, in particular;
- (3) Feasibility of a unified quantum-chemical description both of pericyclic and of ionic reactions in terms of direct and indirect interorbital interactions (cf. the recent studies of  $S_N2$  [36,37] and of  $Ad_E2$  [38] processes).

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