ELECTRON REORGANIZATION IN CHEMICAL REACTIONS. BOND ORDER CONSERVATION *vs* MULTICENTER BONDING IN THE COURSE OF CHEMICAL REACTIONS

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The conditions underlying the applicability of the empirical BEBO relationship were analyzed and discussed. It has been shown that the relationship holds for reactions in which the electron reorganization can satisfactorily be described by the classical structural theory as a simple shift of bonds. On the other hand, if the electron reorganization is more complex, the BEBO relationship is likely to fail. In these cases, the description of the structure of the transition state requires to invoke the concept of multicenter bonding.

Key words: Bond energy–bond order; Multicenter bonding; Bond order conservation; Pair population analysis; Bond theory; Transition states.

Chemistry is the science of molecular change and the study of structural transformations accompanying the conversion of the reactants into the products is one of the most ultimate goals of chemistry. This is why a lot of effort was devoted to the elucidation of the factors governing the course of such transformations. Although a lot of understanding was already brought by the classical structural theory depicting the shifts of chemical bonds with the well-known “curved arrow” formalism, the real understanding of the physical principles governing the chemical reactions came only with the advent of the quantum theory; during the years of its development a great progress towards the understanding chemical reactivity was achieved. To remind only few examples, the Eyring theory of absolute reaction rates[1], the Woodward–Hoffmann rules[2] or Bader‘s theory of atoms in molecules[3] can be mentioned. Although it is true that quantum chemistry is in principle able to describe the structure and the energies of all the species participating in chemical reactions, whether stable or transient, such a description is frequently quite cumbersome and lacks the simplicity and transparency of simple models which are inherently linked with the human thinking and as such are of vital importance for the true understanding of the nature of the reaction event. This is why so many simple qualitative models of reactivity was proposed. Among them it is possible to mention, *e.g.*, the principle of the minimal structural change[4] or the least-motion principle[5], the Bell–Evans–Polanyi relationship[6], the Hammond postulate[7] and others. Closely related to these simple models is also the so-called bond energy–bond order (BEBO) relationship[8,9] which attempts to characterize the course of chemical transformation in terms of the changes of the bond orders. Although the bond orders, or closely related bond indices[10–14] found in recent years a lot of interesting applications in the study of chemical reactions[15–20], greater impact of these studies is still a bit hindered by the fact that the BEBO relationship, which is the basis of all these applications, is only of empirical nature. For this purpose, a lot of effort was devoted to putting this relationship on more sound theoretical basis. Our aim in this study is to contribute to these efforts and to attempt to throw some new light on the factors governing the validity of the BEBO relationship. The basis of our approach is the recently introduced formalism of the so-called pair population analysis[21] in terms of which an extremely simple and transparent picture of chemical structure can be given.

Although the first applications of this analysis referred to stable molecular species, there is no obstacle preventing its extension to species lying along the reaction path and as it will be shown below, such an extension is indeed able to stress at least some of the factors underlying the validity of the BEBO relationship. In the following part, the applications of the pair population analysis to reacting systems will be reported and the conditions necessary for the validity of the BEBO relationship will be discussed.

THEORETICAL

The methodological basis of our approach is the recently introduced formalism of the so-called pair population analysis and of its subsequent extensions[21–24]. Although the principles of this analysis are satisfactorily described in previous studies[21–23], we consider it worthwhile to recapitulate briefly the basic ideas of this approach to the extent necessary for the purpose of the present study. The basic quantity of the analysis is the so-called pair density which is defined as a diagonal element of the (spinless) second-order density matrix[25].

$$\rho(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{N(N-1)}{2} \int \Psi^2(1, 2, 3 \ldots N)\, \mathrm{d}\sigma_1\, \mathrm{d}\sigma_2\, \mathrm{d}x_3 \ldots \mathrm{d}x_N \qquad (1)$$

This density can straightforwardly be expressed in the form of expansion in the AO basis:

$$\rho(\boldsymbol{r}_1,\boldsymbol{r}_2) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} \Omega_{\alpha\beta\gamma\delta}\, \chi_\alpha(1)\, \chi_\beta(1)\, \chi_\gamma(2)\, \chi_\delta(2) \;, \qquad (2)$$

where the density itself is represented by the four-index matrix Ω. In previous study[21] we have shown that this equation can substantially be simplified if the original orbital-based expansion is replaced by the alternative expansion in the basis of two-electron functions, the so-called geminals.

$$\rho(\boldsymbol{r}_1,\boldsymbol{r}_2) = \sum_{\alpha} \sum_{\beta} \Gamma_{\alpha\beta}\, \lambda_{\alpha}(1,2)\, \lambda_{\beta}(1,2) \tag{3}$$

As demonstrated in the study[21], if these geminals are formed as symmetric or antisymmetric combinations of orbital products,

$$\begin{aligned} \lambda_{\alpha,\alpha}(1,2) &= \chi_{\alpha}(1)\, \chi_{\alpha}(2) \\ \lambda^{+}_{\alpha\beta}(1,2) &= \frac{1}{\sqrt{2}}(\chi_{\alpha}(1)\, \chi_{\beta}(2) + \chi_{\alpha}(2)\, \chi_{\beta}(1)) \\ \lambda^{-}_{\alpha,\beta}(1,2) &= \frac{1}{\sqrt{2}}(\chi_{\alpha}(1)\, \chi_{\beta}(2) - \chi_{\alpha}(2)\, \chi_{\beta}(1)) \end{aligned} \tag{4}$$

the matrix Γ is block diagonal with one block describing singlet and the other the triplet states of electron pair.

$$\Gamma = \Gamma^{S} \oplus \Gamma^{T} \tag{5}$$

The fact that the matrix Γ, representing the pair density in geminal basis is a normal two-index matrix similar in form to the expansion of first-order density matrix in the AO basis allowed us to apply the idea of the Mulliken population analysis[26] to the analysis of pair density. Using this parallel, the pair density can be decomposed into mono- and biatomic populations:

$$\int \rho(\boldsymbol{r}_1,\boldsymbol{r}_2)\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = \sum_{A} \Pi_{AA} + \sum_{A<B} \Pi_{AB} \quad . \tag{6}$$

Besides this straightforward parallel with the Mulliken population analysis, there are, however, also some differences. These differences are due to the specific block-diagonal form of the matrix Γ which allows to calculate separate singlet and triplet pair populations. While these individual singlet and triplet pair populations are difficult to interpret, a simple physical meaning can be attached to another kind of populations, the so-called “effective” pair populations defined as[21–24]

$$\begin{aligned} \Pi^{\text{eff}}_{AA} &= \Pi^{s}_{AA} - \frac{1}{3}\Pi^{t}_{AA} \\ \Pi^{\text{eff}}_{AB} &= \Pi^{s}_{AB} - \frac{1}{3}\Pi^{t}_{AB} \quad . \end{aligned} \tag{7}$$

The usefulness of these effective pair populations for the elucidation of molecular structure arises from the close parallel between the effective pairs and the chemical bonds disclosed and discussed in previous studies[21–23]. The basis of this parallel is the interesting normalization relation

$$\sum_{\mathrm{A}} \Pi_{\mathrm{AA}}^{\mathrm{eff}} + \sum_{\mathrm{A<B}} \Pi_{\mathrm{AB}}^{\mathrm{eff}} = \frac{N}{2} \tag{8}$$

which says that the sum of all mono- and biatomic effective pair populations equals to $N/2$, which, for the molecule with N electrons, is just the number of bonds plus free and core electron pairs. This normalization is also the basis of our present approach to the theoretical justification of the BEBO relationship. This justification is based on the fact that within the framework of the SCF approximation, which is of our concern here, the effective pair populations are equivalent to the so-called Wiberg or bond indices[11], which are now generally accepted to be an appropriate measure of bond order (bond multiplicity)

$$\begin{aligned} \Pi_{\mathrm{AB}}^{\mathrm{eff}} &= W_{\mathrm{AB}}/2 \\ \Pi_{\mathrm{AA}}^{\mathrm{eff}} &= W_{\mathrm{AA}}/2 \quad . \end{aligned} \tag{9}$$

It is generally valid that irrespective of the nature of the bonded atoms, the bond indices for single, double or triple bonds are close to 1, 2 and 3, respectively, while for classically non-bonded atoms the values are practically negligible[21–23]. As a consequence, the exact relation (*8*) can frequently be simplified to the form

$$\sum_{\mathrm{A}} \Pi_{\mathrm{AA}}^{\mathrm{eff}} + \sum_{\mathrm{A<B}}^{\mathrm{bonded}} \Pi_{\mathrm{AB}}^{\mathrm{eff}} \approx \frac{N}{2} \ , \tag{10}$$

where the summation runs not over all pairs of atoms but only over those pairs which are directly bonded in the classical formula. In this form, the approximate normalization was recently used for the evaluation of the accuracy of the classical Lewis electron pair model of chemical bond[21–23,27].

Our aim in this study is to extend the applicability of the approximate normalization (*10*) beyond the class of stable molecular species and to apply it to the description of structural reorganization in the course of chemical reactions. The basic idea of such an extension arises from the classical structural theory in which the structural reorganization is described as a shift of chemical bonds (electron pairs) from the positions characteristic of the starting reactant to the positions in the final products. Within this model, the chemical reaction can be regarded as a flow of electron pairs from initial to final positions. Such a picture of continuous bond interchange, complemented with the requirement of the conservation of “overall amount of bonding” is the intuitive rationale lying behind the so-called BEBO relationship[8,9]. Our aim in this study is to demonstrate that the validity of this empirical relationship can straightforwardly be evaluated on the basis of the approximate normalization (*10*). For this purpose, let us analyze the individual terms in Eq. (*10*). First of them involves the sum of monoatomic pair populations. These populations have the important property of depending primarily on the type of the atom without being influenced too much by the actual atom neighbours. This implies that on comparing isomeric systems like the reactant, transition state and the product of chemical reaction, this term should remain essentially constant. Further simplification allowing to stress the direct parallel between the approximate normalization (*10*) and the BEBO relationship is based on the well-known empirical fact that chemical reaction usually involves only few actively participating bonds while the rest of the molecule remains more or less untouched. This allows to rewrite the second term of Eq. (*10*) in the form,

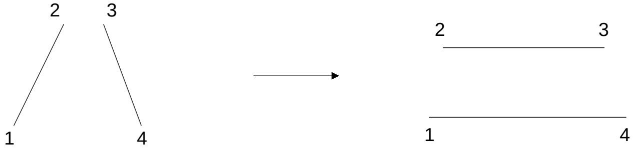
$$\sum_{A<B}^{\text{bonded}} \Pi_{AB}^{\text{eff}} = \sum_{A<B}^{\text{active}} \Pi_{AB}^{\text{eff}} + \sum_{A<B}^{\text{inactive}} \Pi_{AB}^{\text{eff}} \qquad (11)$$

in which the summation over active and inactive bonds is distinguished. If now we take into account that for such closely related systems like the reactant, transition state and the product, the summation over the inactive bonds should again remain nearly constant, the original approximate normalization (*10*) can be rewritten in the form (BEBO sum)

$$\sum_{A<B}^{\text{active}} \Pi_{AB}^{\text{eff}} \approx \frac{N}{2} - \text{const} \qquad (12)$$

which is just the desired simple mathematical formulation of the bond order conservation (BEBO relationship) in the course of chemical reactions.

Thus, for instance, if the chemical reaction can schematically be described by a cyclic shift of bonds like in Scheme 1,



SCHEME 1

the accuracy of the BEBO relationship can straightforwardly be evaluated by comparing to what extent the constancy of the BEBO sum (*13*) is maintained along the reaction path.

$$\Pi_{12}^{\text{eff}} + \Pi_{23}^{\text{eff}} + \Pi_{34}^{\text{eff}} + \Pi_{14}^{\text{eff}} \approx \text{const} \tag{13}$$

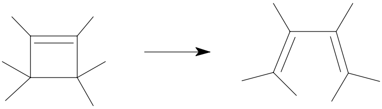
Similar relations can, of course, be also written down for other reaction schemes so that the above method can be regarded as entirely general. The BEBO relationship can be expected to be valid if the approximate formula (*12*) is satisfied with acceptable accuracy during the whole process. On the other hand, greater deviations from the approximate relationship (*12*) indicate the failure of the BEBO relationship.

Let us now look at the situation where such a failure could appear. For this purpose, let us refer again to Scheme 1. As suggested by the scheme, if the reaction proceeds as a simple shift of bonds, the only non-vanishing pair populations are those involving the active bonds Π_{12}, Π_{34}, Π_{23} and Π_{14}. If, however, the chemical reaction involves a more complex electron reorganization so that some pair populations between directly non-bonded atoms can no longer be neglected (Π_{13}^{eff}, Π_{24}^{eff} in our case), the validity of the BEBO relationship can seriously be questioned. In recent study[27] the situation where non-vanishing pair populations appear also between directly non-bonded atoms was analyzed in detail and it was found that this is typical of the systems with three- or multicenter bonding. In view of this result, it is possible to assume that the deviations from the BEBO relationship can appear in situations where the multicenter bonding can be expected to play a role in the transient structures along the reaction path. In the following part, the validity of the above assumption as well as the general conditions for the validity of the BEBO relationship will be discussed by analyzing several selected reactions. The studied systems involve the thermally allowed conrotatory cyclobutene to butadiene ring opening, the *supra-supra* Diels–Alder addition of ethene to butadiene and the HNC → HCN isomerization. The calculations were performed by the semiempirical AM1 method[28] included in the MOPAC package[29]. In all cases the transition states were localized as saddle points on the PE hypersurface and the intrinsic reaction path (IRC) was followed at both sides of the barrier to obtain the structures along the reaction path.

In the following part, the results of our calculations will be reported.

RESULTS AND DISCUSSION

The first system we decided to study using the above approach was the thermally allowed conrotatory ring opening of cyclobutene to buta-1,3-diene (Scheme 2).



SCHEME 2

The calculated heats of formation of the reactant, product and the transition state agreed with the reported literature data[30] and are summarized in Table I. In order to demonstrate the validity of conditions underlying the transformation of the universal normalization condition (*8*) into the form of the BEBO relationship (*12*), the values of the sums of monoatomic pair populations as well as the sum of biatomic pair populations over the inactive bonds are also included in Table I. As can be seen, both sums are virtually constant for all three crucial structures so that the conditions for the BEBO relationship to hold are satisfied. That this is indeed the case can also be seen from the values of the BEBO sum (*13*) in the same table. Another independent proof demonstrating the fact that in keeping with the BEBO relationship the reaction proceeds as a simple cyclic shift of bonds is apparent from Fig. 1 depicting the changes in the bond order of the active bonds along the IRC. Clearly, the complementarity between the bond orders of disappearing and newly formed bonds is nearly ideal in this case so that

TABLE I
AM1-calculated characteristics of the thermally allowed conrotatory cyclobutene → butadiene ring opening

Quantity	Reactant	Transition state	Product
ΔH_f, kJ/mol	128.3	339.0	191.4
$\sum_{A} \Pi^{eff}_{AA}$	5.586	5.602	5.592
$\sum_{A<B} \Pi^{eff}_{AB(inactive)}$	5.337	5.292	5.310
BEBO sum	2.536	2.448	2.448

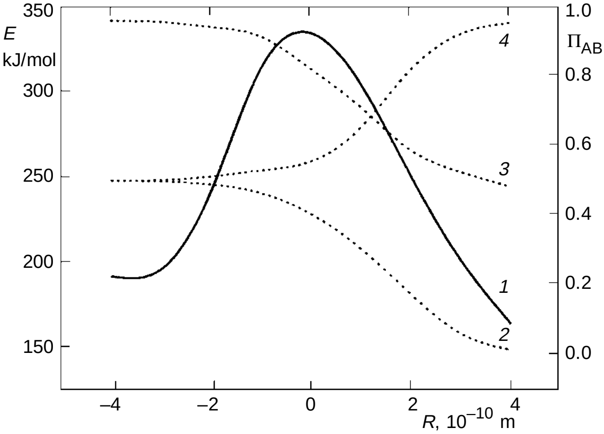


FIG 1.
Variation of AM1-calculated energy and pair populations of disappearing and newly formed bonds in thermally allowed cyclobutene to butadiene ring opening along the concerted reaction path. The reaction coordinate (*R*) was calculated as the intrinsic reaction coordinate. *1* Energy; *2* Π_{14}; *3* Π_{23}; *4* $\Pi_{12} = \Pi_{34}$

the validity of the BEBO relationship is evident. Another system where the BEBO relationship is satisfied is the thermally allowed *s* + *s* butadiene-to-ethene cycloaddition (Diels–Alder reaction). The reactant, product and the transition state were again localized on the PE hypersurface for this system, the resulting values are summarized in Table II. In order to check to what extent the conditions necessary for the validity of the BEBO relationship are satisfied, the sums of monoatomic as well as inactive bond biatomic pair populations are also summarized in Table II. These sums are again virtually constant for all three crucial structures and hence the relationship holds.

As an example of the system where the BEBO relationship is not satisfied was chosen the simple HNC → HCN isomerization. The calculations on this system were again performed by the AM1 method and the resulting heats of formation for the reactant, product and the transition state are summarized in Table III. In the same table, the values of the sum of monoatomic pair populations for the above three crucial structures are also included. Clearly, the requirement of the constancy of this sum is not satisfied and the BEBO relationship is violated in this case. This can also be seen from the comparison of the complementary BEBO sum which displays much greater variation than in the previous cases. Since the systems violating some general rules are usually more interesting that those satisfying them, we decided to analyze this system in more detail. The first indication of the specificity of this system already follows from the comparison of the variation of bond orders along the reaction path (Fig. 2). As can be seen, the corresponding curves do not display such an ideal complementarity as in the previous case and in particular the Π_{CN} pair population behaves counter-intuitively in some region. The crucial role in understanding this unusual behaviour belongs to our previous observation[27] that the systems having non-negligible pair populations Π_{AB}, Π_{BC}, Π_{CA} between three adjacent atoms A, B, C (which is just our case here) usually display three-center bonding. For the detection of this bonding, the formalism of the so-called non-linear pair population analysis was recently proposed[31,32] and in order to

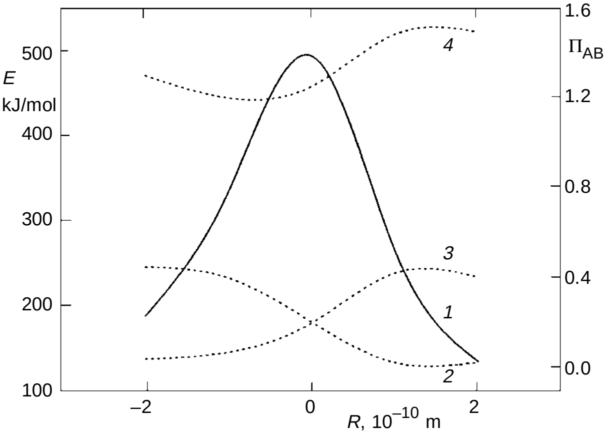


FIG. 2.
Variation of AM1-calculated energy and pair populations of disappearing and newly formed bonds in the HNC → HCN isomerization along the reaction path. Reaction coordinate (*R*) was calculated as the intrinsic reaction coordinate. *1* Energy; *2* Π_{CH}; *3* Π_{NH}; *4* Π_{CN}

check whether this three-center bonding operates in the case of the HNC → HCN isomerization, the non-linear analysis was applied to this system. The results of such an application are displayed in Fig. 3 which depicts the variation of the calculated three-

TABLE II
AM1-calculated characteristics of the thermally allowed *s* + *s* Diels–Alder reaction

Quantity	Reactant	Transition state	Product
ΔH_f, kJ/mol	196.9	293.4	–42.6
$\sum_{A}\Pi_{AA}^{eff}$	8.620	8.632	8.608
$\sum_{A<B}\Pi_{AB(inactive)}^{eff}$	8.258	8.071	8.236
BEBO sum	3.427	3.301	3.431

TABLE III
AM1-calculated characteristics of the HNC → HCN isomerization

Quantity	Reactant	Transition state	Product
ΔH_f, kJ/mol	204.0	494.9	130.0
$\sum_{A}\Pi_{AA}^{eff}$	3.257	3.315	3.054
BEBO sum	1.742	1.685	1.947

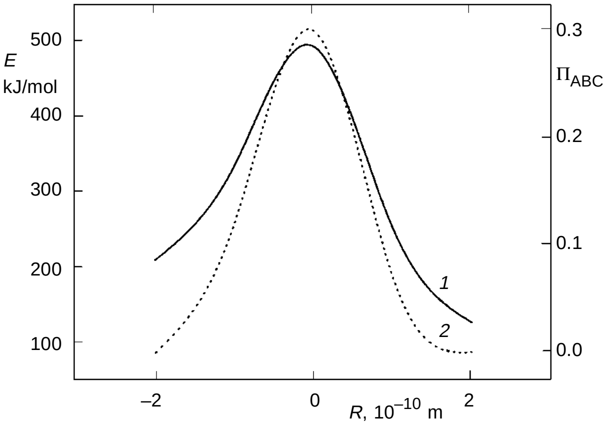


FIG. 3
Variation of AM1-calculated energy barrier (*1*) and Π_{HCN} three-center bond index (*2*) in the HNC → HCN isomerization along the reaction path. Of interest is the nearly coincidence between the position of the transition state and of the structure with the strongest three-center bond. Reaction coordinate (*R*) was calculated as the intrinsic reaction coordinate

center bond index (Π_{HCN}) along the reaction path. As can be seen, the values of this index are quite negligible for the initial HNC and the final HCN (quite in accord with the expectation) but during the process, the role of the three-center bonding dramatically increases and for the transient structures in the vicinity of the transition state, the index becomes quite considerable. This suggests that the description of the structure of the transition state would require to invoke some three-center bonding. Here it is worth mentioning that if the non-linear analysis is applied to reactions satisfying the BEBO relationship (butadiene–cyclobutene cyclization, Diels–Alder reaction), all multicenter pair populations are negligibly small so that there is no multicenter bonding in these cases.

Other potential candidates for violation of the BEBO relationship are forbidden pericyclic reactions and it would certainly be interesting and useful to apply the pair population analysis to this type of processes. Such an application relies, however, on the availability of correlated pair densities which for such type of systems are necessary to describe the electron reorganization properly. Since, however, these correlated pair densities are not readily available from existing quantum chemical programs, the studies dealing with the electron reorganization in forbidden reactions have been rather scarce so far. Nevertheless, the preliminary results obtained and discovered in existing model studies[33,34] are interesting enough to warrant further investigations on these systems.

Summarizing the above results, it is perhaps possible to conclude that the BEBO relationship can be expected to hold for reactions for which the electron reorganization proceeds by a cyclic shift of bonds like in alowed pericyclic reactions. On the other hand, if such a picture of the bond interchange is not applicable, the BEBO relationship can be expected to fail and multicenter bonding is likely to operate in transition states of such reactions.

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