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Electron Reorganization in Allowed and Forbidden Pericyclic Reactions: Multicenter Bond Indices as a Measure of Aromaticity and/or Anti-aromaticity in Transition States of Pericyclic Electrocyclizations

Marcos Mandado[a,*] and Robert Ponec[b]

[a] *Department of Physical Chemistry, University of Vigo, As Lagoas (Marcosende) sn, 36310 Vigo, Galicia, Spain*

[b] *Institute of Chemical Process Fundamentals, Academy of the Sciences of the Czech Republic v.v.i. Prague 6, Suchdol 2, 165 02, Czech Republic*

*Corresponding author. fax: (+34) 986812321, e-mail address: mandado@uvigo.es

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Abstract

The multicenter bond indices, recently proposed as quantitative measures of the cyclic delocalization in aromatic systems, have been applied to characterize the differences in the nature of the electron reorganization in a series of allowed and forbidden electrocyclic reactions of linear neutral polyenes of general formula C_nH_{n+2} and related charged systems of formula $C_nH_{n+2}(+)$ and $C_nH_{n+2}(-)$ for n ranging from 4 to 7. The proposed methodology, which is based on the monitoring of the variation of the extent of cyclic delocalization along the concerted reaction paths, is shown to be completely consistent with the empirical Evans/Dewar classification anticipating aromatic transition states for allowed and antiaromatic transition states for forbidden electrocyclic reactions. Although the study reports the results of the analysis of electron reorganization just for the above mentioned particular class of electrocyclic reactions, the proposed approach is completely general and its conclusions remain valid for any pericyclic reaction.

Introduction

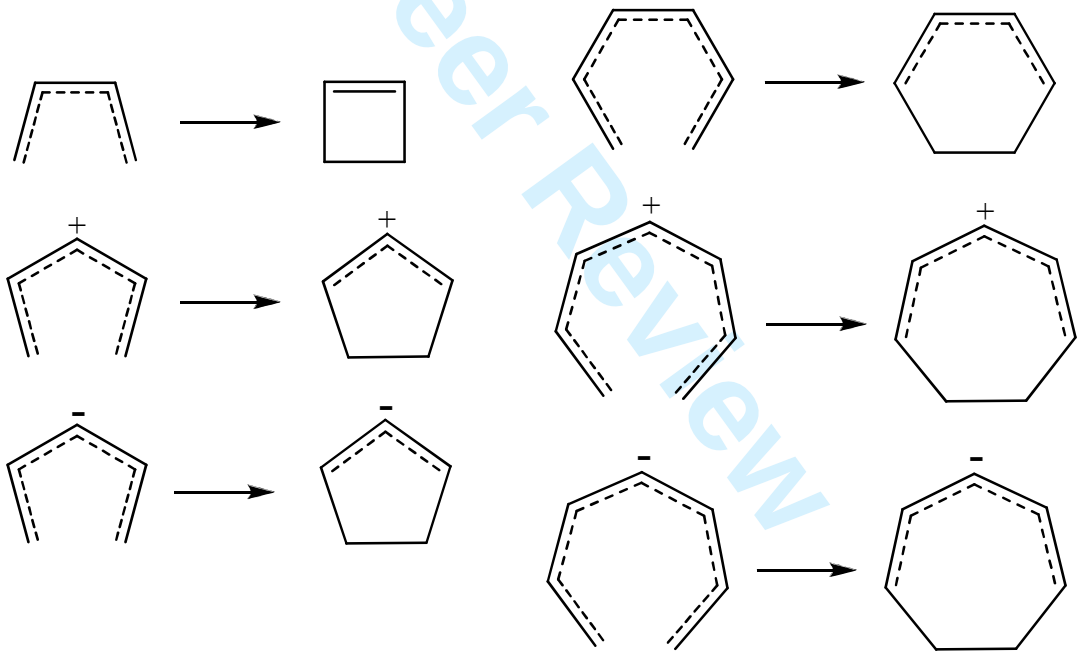
The generic name pericyclic reactions involves the whole class of processes whose typical feature is that the accompanying electron reorganization can formally be described as a cyclic exchange of the bonds. Besides undeniable and unprecedented importance of these reactions as an extremely versatile tool of synthetic organic chemistry, these reactions have also remarkably contributed to the progress of the chemical theory exemplified by the formulation of Woodward-Hoffmann rules.[1] Although the original formulation of W-H rules relates the observed stereospecificity of pericyclic reactions to the molecular symmetry, the fact that eventual deviations from the required high symmetry, induced, e.g., by the substitution, have little effect on the validity of these rules initiated a wealth of studies aiming at the elucidation of the origin of the remarkable universality of W-H rules. These studies resulted in nowadays widely accepted opinion that the decisive role in the formulation of selection rules belongs to orbital topology rather than to orbital symmetry.[2-8] One of the approaches at the topological reformulation of W-H rules is represented by the Dewar's concept of the aromaticity of transition states.[9] According to this concept, inspired by the earlier study by Evans and Warhurst,[10] who noticed that the transition states of Diels-Alder reactions are topologically equivalent (isoconjugated) with benzene, the thermally allowed pericyclic reactions proceed via aromatic transition states. This simple idea has subsequently found an independent theoretical support by Aihara[11] and Van der Hart et al[12] and, more recently, also in our previous studies,[13,14] in which the assumed aromaticity of transition states for allowed reactions (as well as anti-aromaticity for the forbidden ones) has been demonstrated using the so-called molecular similarity indices.[15-18] Although the predictions of the above similarity approach has been shown to completely reflect the anticipations of Dewar`s classification, the fact that the

approach was formulated at the level of HMO-theory raises, of course, the question of the reliability of the predictions based on such a simple approach. Because of importance of the problem, the predictions of Dewar`s classification have recently been discussed using traditional aromaticity measures such as exaltation of magnetic susceptibilities[19,20], ^{1}H NMR chemical shifts[20,21], nuclear independent chemical shifts (NICS)[19,22], PDI[23], FLU[23] etc. Although some of these measures proved to be inadequate,[23] the aromaticity of the transition states of allowed pericyclic reactions seems to have found clear support in the studies based on the use of magnetic aromaticity measures like NICS.[19,22] A more detailed review of these methods can be found in a special issue of Chemical Reviews.[24]

Our aim in this study is to complement these earlier theoretical studies by additional theoretical insights provided by the recently proposed approach based on the exploitation of the so-called multicenter bond indices (MCI).[25-30] These indices, that characterize the extent of the cyclic delocalization, were proposed in past few years as a new quantitative measure of aromaticity in a series of polycyclic aromatic hydrocarbons,[31-39] and because the extended cyclic delocalization can also be assumed to be present in the transition states of concerted pericyclic reactions, it seems attractive to extend the applicability of multicenter bond indices beyond the scope of the traditional applications also to the quantitative evaluation of the Evans/Dewar‘s principle. The first study dealing with the application of this approach was recently reported by one of us,[40] where a non-pericyclic reaction (electrophilic aromatic substitution) was also investigated for the sake of comparison. In this paper we report further systematic extension of this approach to wider series of pericyclic reactions so as to provide additional theoretical insights into the nature of the electron reorganization not only in allowed, but, to some extent, also in forbidden pericyclic reactions.

To address this task, the electron reorganization in the course of these reactions has been characterized by the detailed monitoring of the variation of multicenter bond indices as the indicators of aromaticity and/or anti-aromaticity along the concerted reaction path of wide series of electrocyclic reactions involving ring-closing reactions of neutral linear polyenes of the general formula C_nH_{n+2} for n = 4 and 6 and related charged systems of the formula $C_nH_{n+2}^{(+)}$ and $C_nH_{n+2}^{(-)}$ for odd values of n = 5 and 7. A schematic representation of these electrocyclic reactions is given in Scheme 1.

Marcos, please change the scheme so as to reflect the delocalized nature of the reactants (pentadienyl cation and anion and heptatrienyl cation and anion). The referee was correct in pointing out this inconsistence.



Scheme 1: Schematic representation of the electrocyclic reactions studied.

Theoretical

The multicenter bond indices are the quantities designed for the characterization of the extended delocalization assumed to play the role in the phenomenon of multicenter bonding and as such have found extensive use as a new theoretical tool for the description of such a non-classical bonding.[41-43] The indices were originally introduced[25-28] as mono-, di-, tri- and generally k-centre permutation unique terms resulting from the partitioning of the identity (1), that reflects the idempotency of the density matrix at Hartree-Fock and formally also Kohn-Sham level of the theory.

$$\frac{Tr(PS)^{(k)}}{2^{k-1}} = N = \sum_{A} \Delta_{A}^{(k)} + \sum_{A,B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \ldots \sum_{A<B<C\ldots K} \Delta_{ABC\ldots K}^{(k)} \qquad (1)$$

In this equation (PS) denotes the product of charge-density bond order matrix P and the overlap matrix S and $A,B,C\ldots K$ label individual atoms in the molecule.

Although the bond indices (1) can in principle be used for the description of delocalized multicenter bonding extended over arbitrary number of centers, the practical applicability of such indices is to certain extent restricted due to the presence of the normalization factor $½^{(k-1)}$, owing to which the values of the indices rapidly decrease with increasing k. In order to remedy the above disadvantage, and to make the approach more suitable also to multicenter bonding extended over more centers, we have recently suggested[35] to return to original proposal by Sannigrahi and Kar[27] and to renormalize the original index according to eq. (2)

$$MCI_{ABC\ldots K}^{(k)} = 2^{(k-1)} \Delta_{ABC\ldots K}^{(k)} \qquad (2)$$

Using such a renormalization, the k-center bond index is defined by eq. (3)

$$MCI_{ABC..K}^{(k)} = \sum_{I=1}^{k!} \hat{P}_I \sum_{\alpha\in A}\sum_{\beta\in B}\sum_{\gamma\in C}...\sum_{\kappa\in K}(PS)_{\alpha\beta}(PS)_{\beta\gamma}...(PS)_{\kappa\alpha} \quad (3)$$

in which (*PS*) has the same meaning as in eq. 1, μ, ν, …,ξ refer to basis functions localized at the corresponding atoms and $\hat{P}_I$ is the permutation operator that takes into account all possible k! permutations of the atomic labels.

The above original definition of multicentre index was subsequently generalized[36-40,44-47] into the framework of the quantum theory of atoms in molecules, QTAIM,[48] and within this approach the formula (1) can be rewritten in the form (4)

$$MCI_{ABC..K}^{(k),AIM} = 2^k \sum_{I=1}^{k!} \hat{P}_I \sum_{i}^{occ}\sum_{j}^{occ}...\sum_{k}^{occ}\langle i|j\rangle_A\langle j|r\rangle_B...\langle k|i\rangle_K \quad (4)$$

where $\langle i|j\rangle_X$ denotes the overlap integrals of occupied molecular orbitals *i* and *j* over the domain of the atom X.

$$\langle i|j\rangle_X = \int_{\Omega_x} \varphi_i(r)\varphi_j(r)dr \quad (5)$$

As the identity (1), on which rely definitions of bond indices (Eq. 3 and 4), is valid for Hartree-Fock (and also formally also Kohn Sham) level of the theory and the corresponding multicenter indices can thus straightforwardly be applied for the monitoring of electron delocalization only in allowed reactions, where the above approaches represent a reasonable approximation, the extension of the formalism to

post-Hartree-Fock level of the theory, required for the description of forbidden reactions, was also reported.[29,49,50] As, however, the strictly correlated description requires the knowledge of correlated higher order densities which are not easily available, the approximate description that relies only on the knowledge of the correlated first order density matrix was also suggested as a feasible alternative.[51-55] Within such an approach, the original formula (4) can be generalized in the form (6)

$$MCI_{ABC..K}^{(k),AIM} = \sum_{I=1}^{k!} \hat{P}_I \sum_{i}^{occ} \sum_{j}^{occ} ... \sum_{k}^{occ} n_i n_j ... n_k \langle i | j \rangle_A \langle j | r \rangle_B ... \langle k | i \rangle_K \qquad (6)$$

where n_i, n_j ... n_k denote the occupation numbers of natural molecular orbitals. In the case of the alternative Mulliken-like approach, the definition of k-center bond index (Eq. 3) remains formally unchanged, the only difference is that the charge-density bond order matrix is calculated from the natural orbitals using actual non-integer, occupation numbers.

Computational Details

In order to get a detailed insight into the electron reorganization in the course of pericyclic reactions so as to confront it with the predictions of the empirical Evans/Dewar principle, we have performed a detailed analysis of the potential energy surfaces (PES), of the studied series of reactions. The analysis comprised two steps: first of them involved the localization of the transition states for all the studied reactions on the corresponding PES. In all cases the localized structures have been found to

correspond to true saddle points[1]. After having localized the transition states, the PES analysis was complemented by the intrinsic reaction coordinate (IRC) following whose aim was to characterize the evolution of the cyclic delocalization and/or aromaticity in the course of reaction via the monitoring of the variation of the multicenter bond indices along the corresponding reaction paths.

In the case of allowed reactions, which are known to be less sensitive to the inclusion of the electron correlation, and reasonable description of various molecular properties is provided even by single-determinant RHF and/or Kohn-Sham wave functions[56-61], the calculations have been performed using Gaussian 03 program[62] at B3LYP/6-311++G(d,p) level of the theory.

In the case of forbidden reactions, however, the situation is more complex. These reactions are, namely, known to be much more sensitive to the inclusion of electron correlation[63,64] and their reasonable description requires to go beyond the scope of Hartree-Fock and/or the DFT level of the theory.[63,64] Moreover, in contrast to allowed reactions for which the structures at the top of concerted energy barrier correspond to true saddle points, the character of the PES of forbidden reactions is more complex and the critical structures at the top of concerted energy barrier, localized using constrained search along the hypothetical forbidden pathway, often turns out to be the energy maxima with two or more imaginary frequencies[65,66]. This, of course, prevents the characterization of the reaction in terms of IRC. The only system for which the existence of true transition state (saddle point) in forbidden concerted reaction path was reported is the conrotatory cyclization of hexatriene to cyclohexadiene[67] and for this reason we included this reaction as a representative example demonstrating the nature of

[1] optimized structures and atomic coordinates of the studied transition states are shown in the supporting information

electron reorganization in forbidden reactions. In keeping with that study[67] our analysis was performed at the same level of the theory (CASSCF (6,6)/6-31G(d,p)) with the active space involving all occupied and virtual π molecular orbitals and the electron reorganization along this forbidden concerted reaction path was again followed by the monitoring of the variation of the corresponding multicenter bond indices along the IRC. As the structures along the IRC lack the symmetry plane necessary to distinguish between σ or π molecular orbitals, we have used natural bond orbitals instead of canonical molecular orbitals as initial guess for the CASSCF calculations, so that the bonding and anti-bonding orbitals comprising the active space could be identified unequivocally.

The QTAIM multicenter indices for both the allowed and forbidden reaction paths were calculated at the same level of the theory used for the analysis of the PES in each particular case. However, because of high computational demands of the calculation of QTAIM indices, we also report the comparison of these indices with the analogous quantities calculated using much less demanding Mulliken-like approach which is much more easy to use and which thus could provide a feasible alternative to the reported analysis in other studies. Because of well known failure of the Mulliken population analysis for the basis sets involving diffuse functions,[68] a smaller, but still flexible enough 6-311G(d,p) basis set was used for this alternative approach.

In order to provide a simple qualitative insight into the picture of the electron reorganization provided by the above *ab-initio* description, especially in the case of forbidden reactions where the IRC study was available only for a single reaction, a detailed systematic study of electron reorganization was also performed for a wide series of both forbidden and allowed reactions using the topological approach known as the overlap determinant method, ODM.[18,69-71] Within this approach the electron

reorganization in the course of the reactions is being described by the simple formula ensuring the transformation of the reactant into the product by equation (7)

$$\Phi(\varphi) = \frac{1}{N(\varphi)}(\cos\varphi \cdot \Psi_R + \sin\varphi \cdot \Psi_P) \tag{7}$$

in which the Ψ_R and Ψ_P denote approximate wave functions of the reactant and product respectively and the variable φ varies between 0 and π/2. Based on the above formula, the electron structure of the species along the reaction path is characterized by the first order density matrix (8),

$$P(\varphi) = \int \Phi^2(\varphi) d\xi_1 dx_2 dx_3 ... dx_N = \sum_\mu \sum_\nu [P(\varphi)]_{\mu\nu} \chi_\mu \chi_\nu \tag{8}$$

which has been shown to correctly reflect the dramatic difference in the nature of the electron reorganization in allowed and forbidden pericyclic reactions.[71] This opens the possibility to use the density matrix (8) as a source of structural information for the characterization of the anticipated differences in the extent of the cyclic delocalization along the reaction path via the monitoring of the φ-dependence of the corresponding multicenter bond indices. In addition to such a dependence, the above approach also allows one to characterize the extent of the cyclic conjugation in the transition state via the multicenter indices calculated in each particular case from the density matrix (8) for φ = π/4.

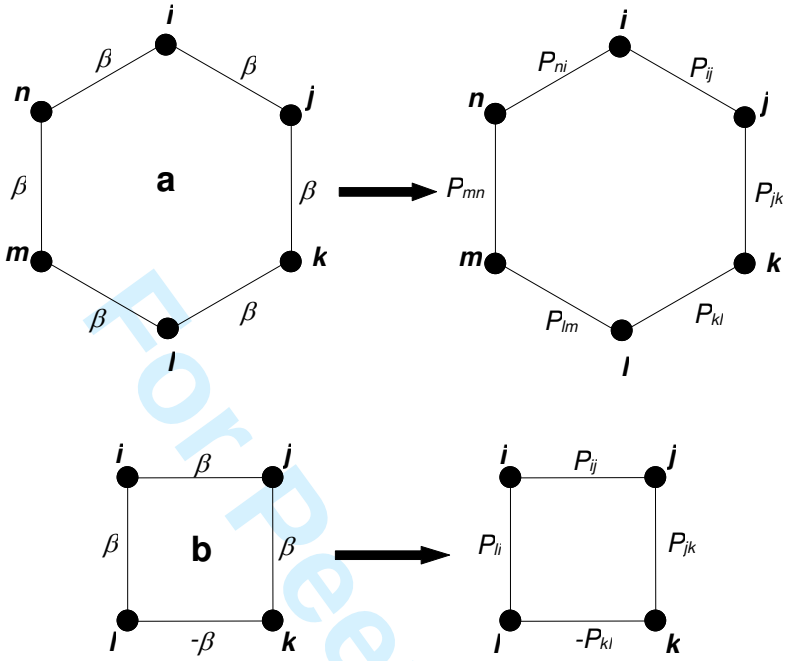
Results and discussion

According to the Woodward-Hoffman rules, the stereochemical preference of allowed electrocyclic reactions involving 4n+2 electrons is the disrotation, while for 4n electron systems the preferred reaction pathway is the conrotation. This change has, of course, its impact on the bonding topology of the corresponding transition states, for which the Evans/Dewar principle requires the switch from the ordinary Hückel- to Möbius-like topology. To demonstrate the effect of the above switch on the nature of electron reorganization during the reaction, the dependence of the calculated multicenter indices on the IRC value for the (allowed) conrotatory butadiene to cyclobutene cyclization and disrotatory transformation of hexatriene to cyclohexadiene, as the representatives of 4n and 4n+2 electron transformations respectively, is depicted in Figure 1. As it is possible to see, the switch of the topology required for the allowed reaction pathways by the Woodward-Hoffmann rules, is reflected in the dramatic difference of the shape of the dependences. Thus, e.g., in the case of 4n+2 disrotatoty hexatriene cyclization, the electron reorganization is characterized by the concave shape of MCI vs IRC plot with the maximum of the cyclic delocalization near the transition state. On the other hand, in the case of 4n-electron conrotatory butadiene to cyclobutene cyclization, the character of the plot is completely opposite; the electron reorganization is associated with the negative values of MCI that near the transition state attain its minima. The same effect of reversal of the MCI vs. IRC dependence on switching from Hückel to Möbius topology and vice versa is also straightforwardly corroborated by the numerical data in Table 1, in which likewise changes in the sign of MCI at the transition states of allowed 4n and 4n+2 pericyclic reactions are clearly reflected. This result is very interesting

since irrespective of the dramatic change in the sign of the bond index, the nature of the electron delocalization in allowed reactions is such that the corresponding transition states display the features typical for aromatic systems. Thus, e.g., Evans/Dewar classification requires the transition state of allowed disrotatory cyclization of hexatriene to cyclohexadiene to be isoconjugated with the aromatic benzene. This anticipated resemblance of the cyclic delocalization in both structures, recently confirmed by the calculated values of aromaticity index NICS,[19,22] is reflected here in the same (positive) sign of the bond index for both the transition state (*ab-initio* index 1.233, ODM index 0.999)) and the benzene as the aromatic "reference" standard (*ab initio* index 1.414, ODM index 1.581). On the other hand in the case of the conrotatory butadiene to cyclobutene transformation, the aromaticity of the transition state (*ab initio* index -1.405, ODM index -1.372) requires it to be isoconjugated with the Möbius cyclobutadiene (ODM index -2.000)[2] and it is important that the negative sign of the corresponding bond indices, typical for Möbius-like systems, is indeed consistent with the aromaticity of the corresponding transition state, independently detected by other aromaticity measures like ^{1}H NMR chemical shifts[21]. The above interpretation of the reversal of MCI vs. IRC plots and their close link to the change of aromaticity rules on the switch of the bonding topology is also straightforwardly corroborated by the simple approach based on the HMO description of Hückel and Möbius like systems. Within this approach, the switch of the bonding topology is straightforwardly achieved by the simple change of the sign of the resonance integral β (Scheme 2) which results in the negative sign of the Coulson bond order between the corresponding atoms of the Möbius cyclic array. As the dominant contribution to the bond index comes from the

[2] ab-initio index cannot be calculated because Möbius cyclobutadiene is a hypothetical structure that can be exactly modeled only at HMO level (Scheme 2b)

product of the bond orders between the pairs of neighbouring atoms on the perimeter of the cyclic array, the sign reversal of the bond index straightforwardly results from the change of the sign of the corresponding bond order.



Scheme 2: Schematic representation of Hückel (a) and Möbius (b) bond topologies in terms of the Hamiltonian matrix elements for cyclic 6-center (benzene) and 4-center (Möbius cyclobutadiene) systems, respectively. The scheme also shows the sign of the corresponding bond order matrix elements.

In addition to providing a simple rationale for the close link between the bonding topology, aromaticity of transition states and the sign of the corresponding MCI, the approximate description of overlap determinant can be shown to correctly describe also the nature of electron reorganization during the whole reaction. The dependence of the calculated MCI on the value of the reaction variable φ are summarized for both butadiene to cyclobutene and hexatriene to cyclohexadiene cyclization in Figure 2 and as it is possible to see from the comparison with the Figure 1, that is based on the actual *ab-initio* data, the overall form of the plots is in both cases the same. The close parallel

between the actual *ab-initio* data and the results of the approximate overlap determinant method is also straightforwardly demonstrated by the tight correlation of the multicenter bond indices characterizing the extent of the cyclic delocalization in the transition state derived from the actual *ab-initio* calculations and the corresponding approximate counterparts based on the topological approach of the overlap determinant method. Such a comparison is displayed in Figure 3 and as it is possible to see, the close parallel is observed both for the "exact" QTAIM indices (Equation 4) and computationally less demanding Mulliken-like indices (Equation 3).

This result is very interesting because the observed close parallel between the indices and the overall plots for allowed pericyclic reactions could hopefully open the possibility to provide similar insights into the nature of the cyclic conjugation also in forbidden reactions, where the actual *ab-initio* data were available only for a single reaction, namely the conrotatory cyclization of hexatriene to cyclohexadiene. The calculated MCI vs. IRC dependence for this reaction is displayed in Figure 4. As it is possible to see, the form of the dependence is in this case completely opposite to what was observed for the allowed reaction and the multicenter index at the transition state is in this case negative, as expected for the Möebius-like TSs (see Tables 1 and 2), but dramatically smaller than that of the allowed reaction. This result, which is again completely consistent with the analogous plot derived for this reaction within the approximate overlap determinant method (Figure 2), is very important as it demonstrates that allowedness and/or forbiddeness of the reactions involving the same number of electrons (4n+2 in our case) is associated with the dramatic differences in the character of electron reorganization induced by the switch of the bonding topology. It is possible to see from the numerical data in Table 2 that the same remains true also for other pairs of allowed and forbidden reactions. A comparison of the values collected in

Table 2 shows, that irrespective of the sign, the absolute values of the indices for allowed reactions are considerably higher than for the forbidden ones. This result is very interesting since it straightforwardly reflects the intuitive expectation associating the extent of the cyclic delocalization in the transition states with the energetic benefits accompanying such a delocalization. From this point of view, larger absolute values of the bond indices for allowed reactions can thus straightforwardly be attributed to larger delocalization induced energetic stabilization of the corresponding transition states. On the other hand, in the case of antiaromatic systems the cyclic delocalization is energetically destabilizing, and the low values of the corresponding bond indices thus in fact reflect the tendency of such systems to minimize the energetic loss due to the destabilizing conjugation. This result is very interesting since contrary to the opposite claims of the authors of the study,[53] the multicenter indices, whether calculated at ODM, Mulliken-like or QTAIM level of the theory, are able to distinguish between the aromatic and antiaromatic systems and, consequently, they provide realistic description of electron reorganization in both allowed and forbidden pericyclic reactions.

Similar differences in the manifestation of the cyclic conjugation were also recently observed in a series of 4n- and 4n+2 annulenes[72]. It was found that in contrast to aromatic 4n+2 annulenes, for which the favorable effect of the cyclic delocalization is reflected in that the (absolute) values of multicenter bond indices are systematically larger than for the corresponding linear structures, the situation for the antiaromatic 4n-annulenes is exactly opposite and the drop in the extent of the cyclic conjugation compared to linear analogue is observed.

Conclusions

The presented analysis demonstrates that the multicenter bond indices, recently suggested as a measure of aromaticity in polycyclic aromatic hydrocarbons can successfully be used to characterize the electron reorganization in the course of allowed and forbidden pericyclic reactions. Consistent with the expectation of this classification it has been shown that irrespective of the switch of the bonding topology required by the Woodward-Hoffmann rules on going from 4n+2 to 4n-electron systems, the transition states of allowed reactions do indeed reflect the typical features of aromatic systems while for forbidden reactions the values of multicenter bond indices accordingly suggests the corresponding transition states to be antiaromatic. Such a conclusion is not, of course, new but in contrast to earlier theoretical studies in which the Evans/Dewar classification has been addressed using simple topological methods, the proposed approach is completely general and can be applied to any pericyclic reaction for which the sufficiently reliable description of the potential energy hypersurface and IRC is available.

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Table 1: Renormalized Mulliken- and QTAIM-MCIs for the TSs of the electrocyclic reactions studied. n represents the number of carbon atoms and N_e the number of π electrons.

N	N_e	Pathway	Topology	Mulliken[a,c]	QTAIM[b,c]
4	4	Conrotatory allowed	Möbius	-1.405	-0.781
5	4	Conrotatory Allowed	Möbius	-1.119	-0.857
	6	Disrotatory allowed	Hückel	1.283	0.422
6	6	Disrotatory allowed	Hückel	1.233	0.642
6	6	Conrotatory[d] forbidden	Möbius	-0.099	-0.055
7	6	Disrotatory allowed	Hückel	0.868	0.561
	8	Conrotatory allowed	Möbius	-1.094	-0.351

[a] Mulliken calculations were performed at the B3LYP/6-311G(d,p) level.
[b] QTAIM calculations were performed at the B3LYP/6-311++G(d,p) level.
[c] Geometries of TSs were optimized at the B3LYP/6-311++G(d,p) level.
[d] CASSCF(6,6)/6-31G(d,p) level was employed for this system.

Table 2: Renormalized MCIs calculated using the overlap determinat method for the "transition states" in the series of electrocyclic reactions studied. n represents the number of carbon atoms and N_e the number of π electrons.

N	N_e	Pathway	Topology	Classification	TS
4	4	Conrotatory	Möbius	Allowed	-1.372
		Disrotatory	Hückel	Forbidden	0.320
5	4	Conrotatory	Möbius	Allowed	-1.061
		Disrotatory	Hückel	Forbidden	0.266
	6	Conrotatory	Möbius	Forbidden	-0.266
		Disrotatory	Hückel	Allowed	1.061
6	6	Conrotatory	Möbius	Forbidden	-0.266
		Disrotatory	Hückel	Allowed	0.999
7	6	Conrotatory	Möbius	Forbidden	-0.217
		Disrotatory	Hückel	Allowed	0.761
	8	Conrotatory	Möbius	Allowed	-0.761
		Disrotatory	Hückel	Forbidden	0.217

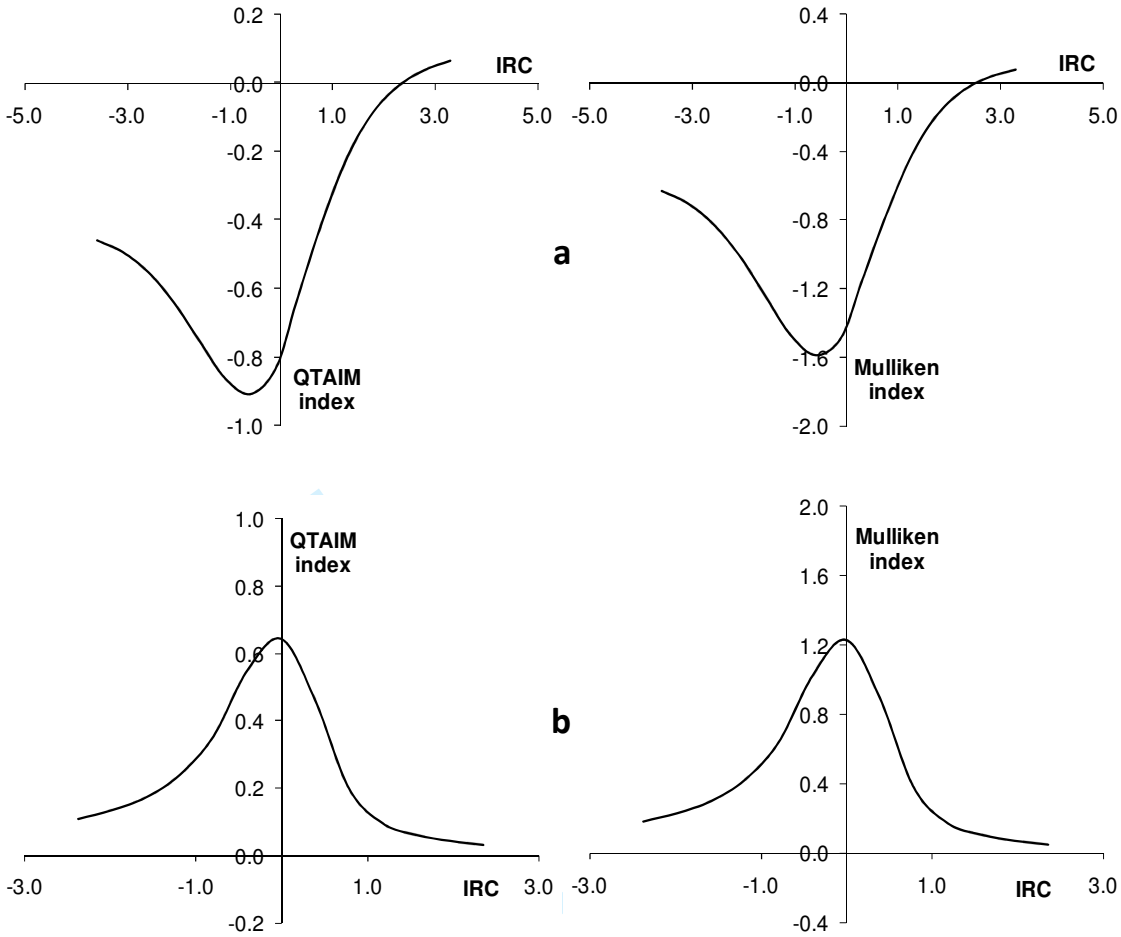

Figure 1: Representations of the renormalized Mulliken- and QTAIM-MCIs calculated at the DFT level along the reaction coordinate for the allowed electrocyclic reactions of butadiene (a) and hexatriene (b). Negative and positive values of the IRC connect to the reactant and product structures, respectively.

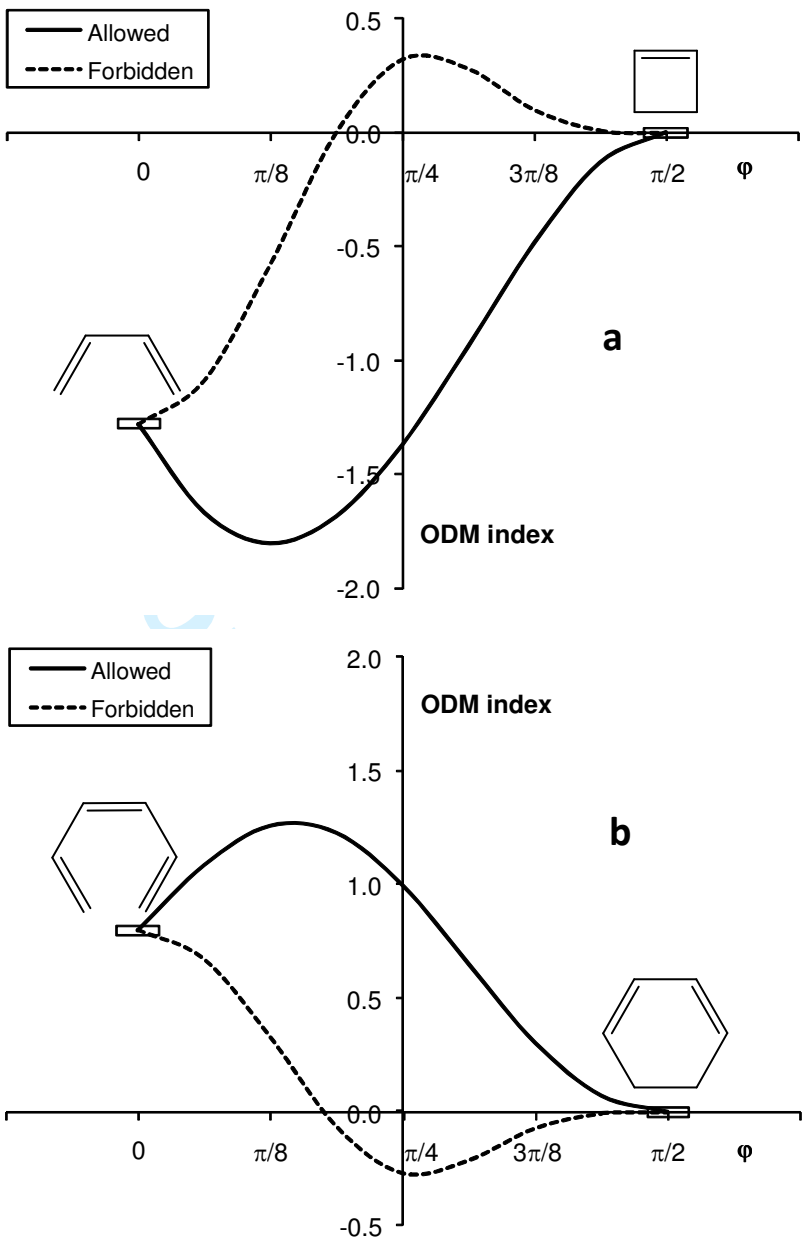

Figure 2: Representations of the renormalized ODM-MCIs along the reaction coordinate for the electrocyclic reactions of butadiene (a) and hexatriene (b).

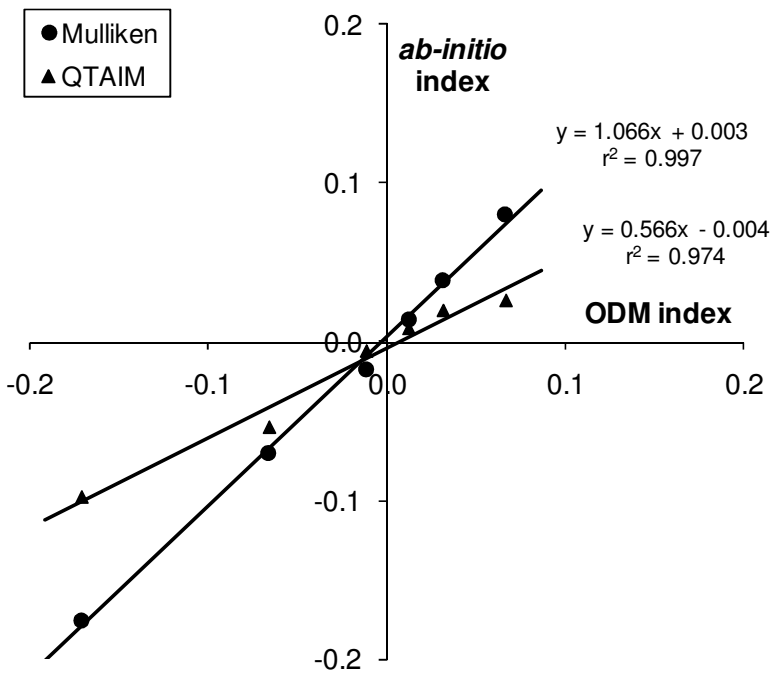

Figure 3: ODM-MCIs vs Mulliken- and QTAIM-MCIs for the TSs of the allowed electrocyclic reactions studied.

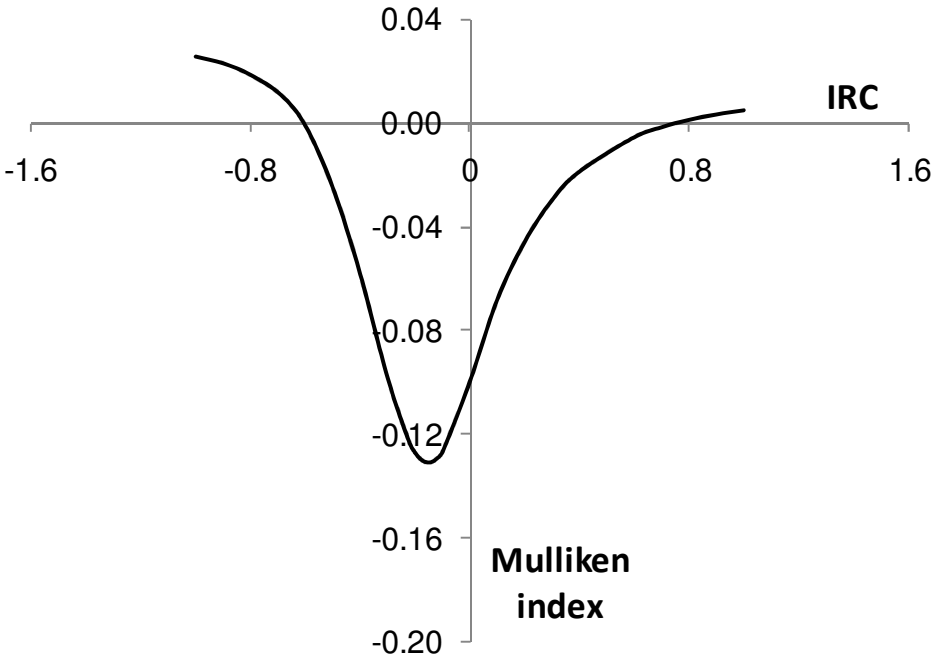

Figure 4: Representation of the renormalized Mulliken-MCIs calculated at the CASSCF(6,6) level along the reaction coordinate for the forbidden electrocyclic reaction of hexatriene. Negative and positive values of the IRC connect to the reactant and product structures, respectively. The scale employed is ten times lower than that of Figure 1b.