Similarity Approach to Chemical Reactivity. Spin Recoupling in Chemical Reactions

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The idea of similarity index was extended to the investigation of the effect of spin recoupling in chemical reactions. The approach was applied at the semiempirical AM1 level to a series of selected pericyclic reactions involving model examples of electrocyclic reactions, cycloadditions and valence isomerizations. Both allowed and forbidden reaction mechanisms were analyzed in each case with the aim to assess the role of spin recoupling in discriminating between these two process types.

INTRODUCTION

The build up of any natural science has always relied on the formulation of simple qualitative concepts in terms of which the observed experimental data can be classified, systemized and understood. As far as chemistry is concerned, the role of the above key concept has been played by the concept of similarity.[1] Although the first applications of similarity ideas were primarily of intuitive nature, the concepts arising from such applications deeply influenced the development of many branches of chemistry. As an example of such an intuitive use it is possible to recall, *e.g.,* the formulation of the Mendeleev periodic law or such basic concepts of organic chemistry as the homological series, functional group, topicity *etc.*, to mention at least some of them. In view of this enormous impact, the concept of similarity has become the subject of systematic investigations and in recent years a lot of effort has been devoted to putting the qualitative and ill-defined concept of similarity on a more sound theoretical basis. The important role in these efforts belongs to the exploitation of the so-called similarity indices, which are the quantities characterizing the similarity of one molecule to another by

quantitatively evaluating the resemblance in their electron structures. These indices, first introduced some time ago by Polansky and Carbo,[2,3] have rapidly found a lot of applications and since then a wealth of related similarity indices and similarity measures have been introduced and applied.[4–16] The scope of these applications is extremely broad and ranges from the rationalization of the design of new biologically active compounds, or new materials, to theoretical applications in the field of chemical reactivity. The framework of these efforts can include, *e.g.,* our previous studies in which the so-called topological similarity index[11,12] was applied to the analysis of various aspects of pericyclic reactivity as the alternative reproduction of Woodward-Hoffmann rules,[11,17] theoretical justification of the Evans/Dewar principle of aromaticity of transition states,[18] or the quantitative evaluation of the role of electron correlation in allowed and forbidden pericyclic reactions.[19]

The aim of this study is to complement the results of our previous studies in the field of pericyclic reactions by looking specifically at the role of electron spin in the process. This is due to the fact that the phenomenon of electron correlation is closely connected with the electron spin (Fermi *vs.* Coulomb correlation[20]), and the specific look at spin recoupling can hopefully be of help in understanding the factors responsible for the discrimination between the allowed and forbidden reactions.

THEORETICAL

The increasing interest in understanding the role of spin structure and spin correlation has stimulated in recent years the efforts to formulate procedures allowing extraction of this specific information from the wave function. Thus, *e.g.,* the method based on the appropriate partitioning of the expectation value of the $\hat{S}^2$ operator was recently proposed and applied[21] within the spin-coupled theory. Stimulated by this approach, we propose here an alternative procedure of the analysis of spin correlation and recoupling based on a combination of appropriate partitioning of the expectation value of the $\hat{S}^2$ operator with the idea of similarity index. The essence of the approach is as follows:

Let us have two molecules A and B and let their structure be described by the corresponding N-electron wave functions Ψ_A and Ψ_B. Based on these wavefunctions, it is possible to introduce the quantities:

$$\mathscr{S}_A(1,2) = \int \Psi_A^*(1,2..N)\,\hat{S}^2\,\Psi_A(1,2..N)\,\mathrm{d}\sigma_1\mathrm{d}\sigma_2\mathrm{d}x_3...\mathrm{d}x_N$$

$$\mathscr{S}_B(1,2) = \int \Psi_B^*(1,2..N)\,\hat{S}^2\,\Psi_B(1,2..N)\,\mathrm{d}\sigma_1\mathrm{d}\sigma_2\mathrm{d}x_3...\mathrm{d}x_N.$$

In these equations, $\hat{S}^2$ denotes the operator of the square of the total spin and integration is performed over the spin coordinates of electrons 1 and 2 and over the spin and space coordinates of the remaining N–2 electrons. These quantities identically satisfy the natural normalization to the expectation values of the $\hat{S}^2$ operator.

$$\int \mathscr{S}_X(1,2)d\tau_1 d\tau_2 = \langle S^2 \rangle_X \qquad (X = A, B)$$

Since each of the quantities $\mathscr{S}_A(1, 2)$ and $\mathscr{S}_B(1, 2)$ separately characterizes the distribution of the spin within individual molecules A and B, it is quite natural to measure the similarity of the corresponding spin distributions by the »spin« similarity index s_{AB}.

$$s_{AB} = \frac{\int \mathscr{S}_A(1,2)\mathscr{S}_B(1,2)d\tau_1 d\tau_2}{\left[\int \mathscr{S}_A^2(1,2)d\tau_1 d\tau_2\right]^{1/2}\left[\int \mathscr{S}_B^2(1,2)d\tau_1 d\tau_2\right]^{1/2}}$$

This definition is thus quite analogous to the definition of the so-called second order similarity index g_{AB},[22,23] the only difference being the use of $\mathscr{S}_X(1,2)$ quantities instead of pair densities. This parallel opens the possibility of using the formalism of the recently proposed geminal expansion of pair densities[24] to the expansion of $\mathscr{S}_X(1,2)$ quantities. Thus, provided geminals λ are defined as properly symmetrized or antisymmetrized orbital products,

$$\lambda_{\alpha\alpha}(1,2) = \chi_\alpha(1)\chi_\alpha(2)$$

$$\lambda_{\alpha\beta}^+(1,2) = \frac{1}{\sqrt{2}}\left[\chi_\alpha(1)\chi_\beta(2) + \chi_\alpha(2)\chi_\beta(1)\right]$$

$$\lambda_{\alpha\beta}^-(1,2) = \frac{1}{\sqrt{2}}\left[\chi_\alpha(1)\chi_\beta(2) - \chi_\alpha(2)\chi_\beta(1)\right]$$

the corresponding expansions have the form

$$S_X(1,2) = \sum_{i,j} Z_{ij}^X \lambda_i(1,2)\lambda_j(1,2).$$

Using these expansions and adopting the same approximations as with the topological similarity index,[12] the spin similarity index s_{AB} can be written as

$$s_{AB} = \frac{\sum\limits_{i,j} Z_{ij}^A Z_{ij}^B}{\sqrt{\sum\limits_{ij}(Z_{ij}^A)^2}\sqrt{\sum\limits_{ij}(Z_{ij}^B)^2}} \qquad (X = A, B).$$

The main advantage of this approach is that, like the original topological similarity index r_{RP}, also the spin similarity index s_{RP} is completely positionally invariant, and so the optimization of the mutual position of both molecules can be avoided. The basic idea of this elimination of positional dependence can be best demonstrated by the original topological index r_{RP}, and although the whole methodology is thoroughly described in the original study,[12] we consider it worthwhile to recall here the basic principles to the extent necessary for the purpose of this study.

The basic idea of topological similarity index arises from the incorporation of the original Carbo's definition of similarity index[3]

$$r_{AB} = \frac{\int \rho_A(1)\rho_B(1)\mathrm{d}\tau_1}{\left[\int \rho_A^2(1)\mathrm{d}\tau_1\right]^{1/2}\left[\int \rho_B^2(1)\mathrm{d}\tau_1\right]^{1/2}}$$

into the framework of the so-called mapping analysis introduced by Trindle.[27] Within this approach, the problem of elimination of multi-centre integrals

$$I_{\mu\nu\lambda\sigma} = \int \chi_\mu^A \chi_\nu^A \chi_\lambda^B \chi_\sigma^B \mathrm{d}\tau,$$

which are the source of the positional dependence of Carbo's index has been solved by introducing the transformation matrix $\boldsymbol{T}$, describing the mutual relation of AO basis sets $\{\chi^A\}, \{\chi^B\}$, on both individual molecules. On the basis of this matrix, together with the subsequent ZDO-like approximation

$$I_{\mu\nu\lambda\sigma} = \delta_{\mu\lambda}\delta_{\nu\sigma}.$$

The original definition of Carbo's index can be rewritten in the final form

$$r_{AB} = \frac{Tr\boldsymbol{P}_A\overline{\boldsymbol{P}}_B}{2N},$$

where $\boldsymbol{P}_A$ and $\boldsymbol{P}_B$ are the usual charge density-bond order matrices of A and B, respectively, and the prime over $\boldsymbol{P}_B$ denotes the unitary transformation with matrix $\boldsymbol{T}$.

$$\overline{\boldsymbol{P}}_B = \boldsymbol{T}^{-1}\boldsymbol{P}_B\boldsymbol{T}.$$

The form of this matrix is then determined from the condition of maximization of the similarity index by the modified procedure proposed by Trindle.[27] This optimized transformation matrix was then used also for analogous transformations required for the calculation of the spin similarity index s_{RP}.

Having recapitulated the main ideas of the adopted approximations, let us proceed now to the application of the above methodology to the analysis

of the problem od spin recoupling in chemical reactions. For this purpose, it is natural, parallel to the philosophy of the similarity approach, to identify molecules A and B with the reactant and the product of the reaction. Index s_{RP} then characterizes the extent of spin reorganization required to convert R to P, quite analogously to the topological similarity index r_{RP}, wich characterizes the extent of electron reorganization[11,12] in the process.

   Because of our interest in pericyclic reactivity, the above approach was applied to the calculation of spin similarity indices s_{RP} for several selected pericyclic reactions involving model examples of electrocyclic reactions, cycloadditions and valence transformations. Since one of the aims of the study was to analyze the differences in the spin recoupling between allowed and forbidden reactions, both allowed and forbidden reaction mechanisms were studied for each proces. Calculations were performed at the semiempirical SCF level using the AM1 method[25] included in the MOPAC package.[26] The calculated values of spin similarity indices are summarized in Table I. Before starting the discussion of these values, it is worthwhile to give a brief comment on a specific feature of the similarity approach. This specificity concerns the interesting fact that, although derived from SCF wave functions, similarity indices provide a reasonable description even in the case of forbidden reactions for which reliable calculations usually require the use of correlated computational methods. The reason for this surprising universality of similarity approach is that the calculation of these indices is based only on the knowledge of the wave function of the reactant and the product

TABLE I

Calculated values of spin similarity indices for a series of selected pericyclic reactions.

Reaction	Mechanism	r_{RP}	s_{RP} (global)	s_{RP} (singlet)	s_{RP} (triplet)
Butadiene $\rightarrow$ cyclobutene	conrotation	0.917	0.841	0.843	0.838
	disrotation	0.905	0.818	0.827	0.811
Hexatriene $\rightarrow$ cyclohexadiene	disrotation	0.915	0.838	0.840	0.834
	conrotation	0.913	0.833	0.838	0.830
Ethene dimerization	s+a	0.899	0.806	0.810	0.803
	s+s	0.914	0.835	0.840	0.829
Diels-Alder reaction	s+s	0.915	0.837	0.840	0.835
	s+a	0.901	0.812	0.816	0.809
Butadiene bicyclobutane	s+a	0.835	0.697	0.705	0.690
	s+s	0.858	0.736	0.740	0.728

Upper mechanism is allowed and the lower forbidden by the Woodward-Hoffmann rules.

only, for which the sensitivity to the quality of calculations is much less and the SCF level of theory is usually acceptable. As a consequence, although the post SCF computational methods are generally to be preferred for forbidden reactions, the similarity approach can be reasonably applied, like *e.g.* the technique of correlation diagrams, to these reactions even at SCF level. The factor that discriminates between allowed and forbidden reactions possible within this approach is the transformation matrix τ, which transforms the wavefunctions of the reactant and the product into the same basis and which differs in both cases due to the geometrical difference of the products of allowed and forbidden reactions. (Scheme I). This matrix, first introduced by Trindle,[27] was subsequently used by us[12] in the definition of the topological similarity index r_{RP}. As a consequence of the differences in transformation matrices, the values of similarity indices for the allowed and forbidden reaction mechanism differ and this difference is just the measure of differences in the extent of electron recoupling during the corresponding reaction mechanisms.
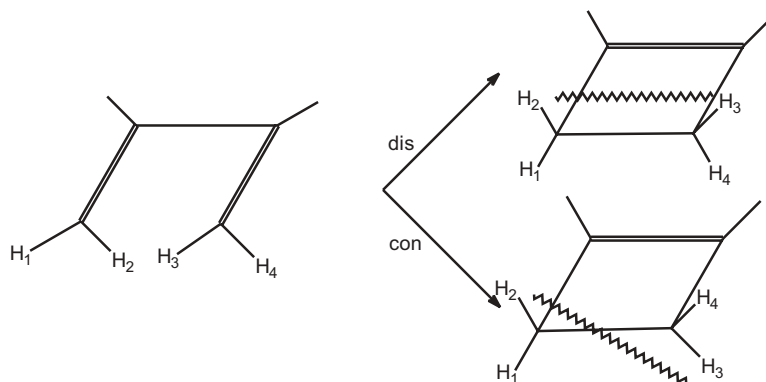
Scheme I

Generally, it holds that higher similarity index values indicate closer similarity in the electron structure of the reactant and the product so that less reorganization is required to transform one structure to another. Such a situation is intuitively expected for allowed reactions. On the other hand, lower similarity index values indicate the necessity of deeper electron recoupling in the transformation and such a situation is typical of the reactions that are forbidden. This interpretation, whose correctness was proved in several previous studies,[11,22] is also the basis of the interpretation of the spin similarity index and the practical application of this index will be reported in the following part.

In addition to providing global information about the extent of spin re-coupling during the reaction, the geminal expansion of the $\mathscr{S}_X(1, 2)$ quanti-ties provides a possibility of an even closer look into the details of spin reor-ganization. Such a possibility arises from the fact that matrix $\boldsymbol{Z}$, repre-senting the $\mathscr{S}_X(1, 2)$ quantity in geminal basis, is block-diagonal with one block corresponding to singlet and the other to triplet states of the electron pair.

$$\boldsymbol{Z} = \boldsymbol{Z}^s \oplus \boldsymbol{Z}^t$$

It is thus possible to calculate not only the »global« spin similarity index s_{RP} but also »partial« spin similarity indices s_{RP}^s and s_{RP}^t for resemblance in in-dividual singlet and triplet blocks of $\boldsymbol{Z}$ matrix, respectively. These indices are also included in the Table.

RESULTS AND DISCUSSION

Let us discuss the conclusions that can be deduced from the calculated values and let us start first by comparing the global similarity indices s_{RP} for allowed and forbidden reaction mechanisms. Based on the above intui-tive interpretation of similarity indices in terms of the ease of allowed and forbidden reactions, it is generally possible to expect that the values of indi-ces s_{RP} should be higher for allowed reactions than for the forbidden ones. This is indeed the case for electrocyclic reactions (butadiene to cyclobutene and hexatriene to cyclohexadiene rearrangement) and the Diels-Alder reac-tion as a representative of cycloadditions. On the other hand , the values for 2+2 ethene dimerization and butadiene to bicyclobutane rearrangement are quite opposite to these expectations and these exceptions could throw some doubts on the general applicability of the similarity approach. For this rea-son, it is necessary to analyze the situation with these two exceptional reac-tions in more detail. Such an analysis starts with a comparison of spin simi-larity index s_{RP} with the »normal« first order similarity index r_{RP} (also in Table I).

As it can be to seen, the trends in both indices are completely parallel and suggest that, contrary to the expectation of the Woodward-Hoffmann rules, the extent of electron and spin reorganization for forbidden s+s mechanism of the two exceptional reactions is lower than for the formally allowed s+a mechanism. In order to explain this apparent discrepancy, it is necessary to realize that the Woodward-Hoffmann rules take into considera-tion only electrons actively participating in the process (4 in this case). As it can be convincingly seen from the values of similarity indices r_{RP} and g_{RP} calculated at this level of approximation,[11,22] the allowed s+a mechanism is indeed easier than the s+s one. The situation with real molecules is, how-

ever, a bit more complex, since extremely large strain can be expected to accompany the s+a ethene dimerization and butadiene-bicyclobutane ring closure. The existence of this strain was already anticipated by Woodward and Hoffmann but their rules, just because of being based on the active electrons only, do not offer any possibility of evaluating the extent of this strain and its eventual mechanistic implications. This, however, becomes possible with the similarity index calculated from semiempirical wave functions where all valence electrons, *i.e.,* the whole molecular skeleton with any possible strain, is taken into account. The presence of such strain is manifested in the decrease of the values of similarity indices, since the ring closure for strained systems will certainly require a deeper electron (spin) reorganization than for the nonstrained ones. That this is indeed the case can straightforwardly be seen from Table I, where the indices for reactions leading to strained cyclo- and bicyclobutane are systematically lower than in the remaining cases. This decrease is observable for both s+s and s+a mechanisms but quite in keeping with the expectations, the decrease is greater for more strained s+a mechanism. This suggests that the reversal of the expected trends in the similarity indices for allowed and forbidden mechanisms in the case of the above two reactions is not an artefact of the approach but it reflects the real physical phenomenon of the ring strain, which leads to that the formally forbidden but less strained s+s mechanism is in fact less electron demanding than the formally allowed but more strained s+a mechanism. Such an interpretation is supported also by the results of rather sophisticated MC-SCF calculations[28] of energy barriers for both s+a and s+s ethene dimerization. These calculations suggest that, despite its allowedness, the barrier for the formally allowed s+a mechanism, is in fact considerably higher than for the formally forbidden s+s mechanism which is clearly a consequence of the huge steric strain accompanying the s+a mechanism. We can thus conclude that, in spite of being seemingly inconsistent with the Woodward-Hoffmann rules, the similarity indices for the above two exceptions are not in fact exceptional but that they reflect the real prohibitive effect of the steric strain of the process. This implies that the parallel the between the extent of electron and spin reorganization suggested by the parallel between similarity index r and the spin similarity index s seems to be valid in this case as well. This result is quite interesting since it clearly demonstrates the important role that belongs to spin recoupling in the process of electron reorganization in the course of chemical reactions.

Having discussed the effect of electron and spin reorganization on the global level, let us now look similarly at the values of »partial« similarity indices for the extent of recoupling for separated singlet and triplet electron pairs. The most important conclusion, which again seems to be valid for all reactions, irrespective of whether forbidden or allowed, is that parallel to what was observed for the »global« index, also the values of spin pure in-

dicea s_{RP}^s and s_{RP}^t for forbidden reactions are generally lower than for the allowed (or easier) ones. This suggests that the extent of spin reorganization in forbidden (or more energy demanding) reactions is also generally higher than in the allowed (or easier) ones for both singlet and triplet pairs. In view of the above conclusions based on the global index, this result is not very surprising, but what is especially useful in this case is the detailed insight into the role of individual singlet and triplet electron pairs in the process. Such an evaluation of the role and the extent of spin recoupling in singlet and triplet electron pairs conveniently complements our previous study in which the alternative partitioning of pair density into contributions from parallel and antiparallel spin pairs was reported.[19] Another interesting conclusion coming from the comparison of individual indices s_{RP}^s and s_{RP}^t is that, irrespective again of the type of reaction, the spin recoupling in singlet pairs is generally lower than in the triplet ones. This result is also quite interesting since it corresponds to what was reported earlier from the analysis of second order similarity indices.[29]

We can thus conclude that the proposed approach opens a new possibility of an intimate insight into the details of spin recoupling in chemical reactions, and we hope that future systematic exploitation of this approach can contribute to a deeper understanding of the role of this recoupling in chemical reactions.

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SAŽETAK

Sličnost u kemijskoj reaktivnosti. Reorganizacija spina u kemijskim reakcijama

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Koncept indeksa sličnosti proširen je na proučavanje reorganizacije spina u kemijskim reakcijama. Taj je pristup primijenjen na razini semiempirijskih AM1 računa na niz odabranih pericikličkih reakcija koje uključuju modelne primjere elektrocikličkih reakcija, cikloadicija i valencijskih izomerizacija. Pojedinačno su analizirani i dopušteni i zabranjeni reakcijski mehanizmi, da bi se utvrdila uloga reorganizacije spina u razlikama između ta dva tipa procesa.