

# Reformulating the Woodward-Hoffmann Rules in a Conceptual Density Functional Theory Context: the Case of Sigmatropic Reactions\*

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**Abstract.** In this contribution, we have investigated the performance of the initial hardness response, a reactivity index from conceptual DFT, in the prediction of the allowed or forbidden character of a series of sigmatropic hydrogen shifts, which are traditionally explained using the famous Woodward-Hoffmann rules for pericyclic reactions. Previously, it was observed that this quantity can be linked to the activation hardness of a chemical reaction and, in this case, thus to the aromaticity of the transition state in these kinds of reactions. It is shown, both by considering approximate reaction coordinates and intrinsic reaction coordinates that the allowed mode of the sigmatropic rearrangement corresponds to the largest value of the initial hardness response, in agreement with earlier work on cycloadditions and electrocyclizations.

**Keywords:** Woodward-Hoffmann rules, sigmatropic reactions, conceptual DFT, hardness

## INTRODUCTION

Density Functional Theory (DFT),<sup>1–7</sup> based on the theorems of Hohenberg and Kohn,<sup>1</sup> uses the electron density  $\rho(\mathbf{r})$  as the basic source of information of an atomic or molecular system instead of the wave function  $\Psi$ . The variational principle formulated in these theorems was turned into a practical working equation by Kohn and Sham,<sup>2</sup> by the introduction of orbitals. In these equations, the only unknown is the so-called exchange-correlation functional  $E_{XC}$ , which contains apart from a kinetic energy part also the non-classical part of the electron-electron repulsion. The search for accurate approximations to this functional is one of the basic themes in fundamental DFT research. Accurate forms of this functional permit the calculation of many atomic and molecular properties with a comparable quality as the more traditional *ab initio* correlated methods but with a much more favourable computational cost.

In addition, DFT has proven to be an ideal framework to sharply define a series of reactivity indices and principles,<sup>3,8</sup> most of which had been introduced previously in chemistry on an empirical basis. Examples of these concepts and principles are the electronegativity, the hardness and the softness, Sanderson's principle of electronegativity equalization and Pearson's Hard and Soft Acids and Bases and

Maximum Hardness Principles. They have been used to rationalize many problems in chemical reactivity.

A famous set of reactivity rules are the Woodward-Hoffmann rules for pericyclic reactions,<sup>9,12</sup> which are reactions involving a cyclic rearrangement of electrons. Examples include cycloadditions, electrocyclizations, sigmatropic rearrangements and chelotropic reactions.<sup>13</sup> Three different approaches for the prediction of the outcome of these reactions are common in the literature; two out of three use symmetry arguments based on signs of either the frontier molecular orbitals or the total wave function of the system.<sup>9–12,14–16</sup> However, none of the chemical concepts introduced in DFT are connected to the phase of the wave function and the question thus arises as to how the Woodward-Hoffmann rules can be recovered from conceptual DFT.

A third method to predict whether a pericyclic reaction is allowed or not was introduced by Zimmerman<sup>17</sup> and uses the concept of the (anti)aromaticity of the transition state. In this approach, reactions with aromatic transition states are asserted to be allowed, while those with an anti-aromatic transition state are considered forbidden. Depending on the number of nodes in the  $\pi$ -system at the transition state of a given mode (*e.g.* conrotatory *vs.* disrotatory, suprafacial *vs.* antarafacial) of the pericyclic reaction, systems can be

\* Dedicated to Professor Zvonimir Maksić on the occasion of his 70<sup>th</sup> birthday.

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classified as either Hückel (zero or even number of nodes) or Möbius (odd number of nodes) systems. Hückel and Möbius systems are aromatic for  $(4n+2)$  and  $(4n)$   $\pi$ -electrons and antiaromatic for  $(4n)$  and  $(4n+2)$   $\pi$ -electrons, respectively.<sup>18–19</sup> Recently, we have found that the concept of initial hardness response (*i.e.* the change of the hardness of the reagents along the initial stage of the reaction) can be used to explain the Woodward-Hoffmann rules in the cases of a series of cycloaddition reactions and electrocyclizations.<sup>20,21</sup> The analysis emphasizes the properties of the reagents and not these of the transition state structures, as studied by Chattaraj *et al.* for some electrocyclic reactions where the Woodward-Hoffmann rules were retrieved in the context of the maximum hardness and minimum polarizability principles.<sup>22</sup> The initial hardness response could be considered as a predictor of the activation hardness, which encapsulates information about the aromaticity of the transition state, which in turn provides a rationale for the Woodward-Hoffmann rules.<sup>20</sup> In addition, we have used a related quantity, the “dual descriptor”<sup>23–25</sup> in the rationalization of these rules for cycloadditions, electrocyclizations and sigmatropic shift reactions.<sup>26</sup>

In this contribution, we will investigate the use of the initial hardness response in detail in the study of sigmatropic shifts. These reactions, depicted in a general form in Figure 1, are concerted reactions in which a group (*e.g.* a hydrogen or an alkyl group) migrates with its  $\sigma$ -bond within a  $\pi$ -framework – an alkene or a polyene; this migration is accompanied by a shift in  $\pi$ -bonds. Depending on the number of  $\pi$ -electrons involved in this process, it will proceed through a suprafacial or antarafacial mode, resulting in a different stereochemical outcome. In the sigmatropic hydrogen shift of linear polyenes, the antarafacial mode corresponds to a Möbius-like ring closure, which relates to an aromatic system when it involves  $(4n)$   $\pi$ -electrons. The suprafacial movement, yielding a Hückel-like ring closure, is aromatic when  $(4n+2)$   $\pi$ -electrons are involved.

In this paper, we will focus on four examples of sigmatropic hydrogen shifts, depicted in Figure 2. For these reactions, we computed the hardness response for the thermal and photochemical sigmatropic reactions along the initial stages of model suprafacial and antarafacial reaction paths. The cases we considered are the [1,3] hydrogen shift in propene, the [1,4] hydrogen shift in the butene cation (both of these reactions are thermally allowed via the antarafacial mode according to the Woodward-Hoffmann rules), the [1,5] hydrogen shift in pentadiene and the [1,6] hydrogen shift in the hexadiene cation (both of these last reactions are thermally allowed via the suprafacial mode according to the rules).

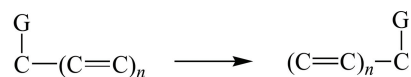


Figure 1. General scheme of a sigmatropic reaction.

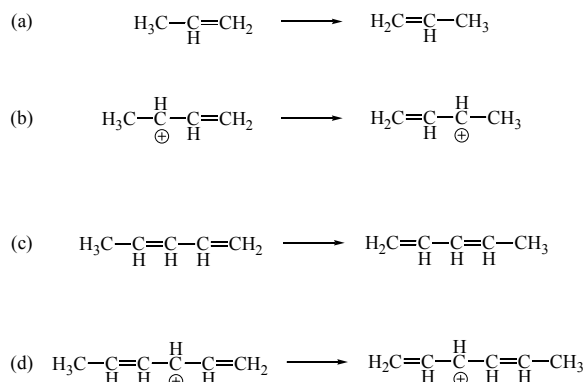


Figure 2. Sigmatropic hydrogen shifts considered in this work.

## THEORY AND COMPUTATIONAL DETAILS

In conceptual DFT or DFT based reactivity theory,<sup>3,8,27–30</sup> reactivity indices are introduced as response functions of the electronic energy  $E$  of the system with respect to either the number of electrons  $N$ , the external potential  $v(r)$  (for an isolated system, this is the potential due to the nuclei) or both. An important quantity, which has been considered numerous times in the study of chemical reactivity and stability, is the chemical hardness,<sup>31–34</sup> defined as the second derivative of the energy  $E$  with respect to the number of electrons  $N$  at a constant external potential, which can be estimated as the difference of the vertical ionization energy and electron affinity of the system:<sup>34</sup>

$$\eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_v \approx I - A \quad (1)$$

An approximate method to compute this quantity was recently introduced by Tozer and De Profis,<sup>35</sup> requiring only the calculation of the neutral and cationic systems and thus avoiding the cumbersome computation of the anionic state:

$$\eta \approx (\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}) + 2(\varepsilon_{\text{HOMO}} + I) \quad (2)$$

where  $\varepsilon_{\text{HOMO}}$  and  $\varepsilon_{\text{LUMO}}$  are the Kohn-Sham orbital energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, obtained using a pure density functional. It can be shown that Eq. (2) corresponds to the operational definition of the hardness (Eq. (1)) using the following approximation for the

electron affinity:

$$A \approx -(\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}) - I \quad (3)$$

This approximate method was shown to give reasonable estimates for the electron affinities of systems possessing metastable anions.<sup>35,36</sup>

In order to compute the hardness for the first excited triplet state, the corresponding ionization energy and electron affinity should be computed, which can readily be done. The vertical electron affinity for a system in the first excited triplet state,  $A(\text{T})$ , was recently shown to be approximated by

$$A(\text{T}) = A(\text{S}) + \Delta E_{\text{ST}} \approx -(\epsilon_{\text{LUMO}}(\text{S}) + \epsilon_{\text{HOMO}}(\text{S})) - I(\text{S}) + \Delta E_{\text{ST}} \quad (4)$$

where  $A(\text{S})$  is the electron affinity of the singlet state, as evaluated by Eq. (3),  $I(\text{S})$  the vertical ionization energy of the singlet ground state and  $\Delta E_{\text{ST}}$  the vertical singlet-triplet gap. The hardness of the first excited triplet state can thus be estimated as

$$\eta(\text{T}) = I(\text{T}) - A(\text{T}) \approx I(\text{T}) + I(\text{S}) + (\epsilon_{\text{LUMO}}(\text{S}) + \epsilon_{\text{HOMO}}(\text{S})) - \Delta E_{\text{ST}} \quad (5)$$

All calculations for this study were performed using the Gaussian 03 program.<sup>37</sup> Geometries, transition states and intrinsic reaction coordinates were obtained at the B3LYP<sup>38</sup>/6-311+G\*\*<sup>39</sup> level (for a detailed account on these types of basis sets, see *e.g.* Ref. 39); single point hardness calculations using Eqs. (2) and (5) were performed using the Perdew, Burke and Ernzerhof (PBE) functional<sup>40</sup> with the same basis set.

## RESULTS AND DISCUSSION

Our previous contributions<sup>20-21</sup> suggested that the Woodward-Hoffmann rules should be recovered in a conceptual DFT framework by means of the initial hardness response along a model reaction path. Sigmatropic hydrogen shifts will be studied for four representative cases: propene, the butene cation, 1,3-pentadiene and the 1,3-hexadiene cation. Before explaining the modelling of the reaction coordinate, it is important to point out that the initial geometries were constructed so that all molecules belong to the  $C_s$  point group. This avoids unnecessary complications of the analysis and is in agreement with the spirit of the original Woodward-Hoffmann work. Absence of imaginary vibrational frequencies after geometry optimisations indicates that the  $C_s$  conformation is situated at a minimum on the

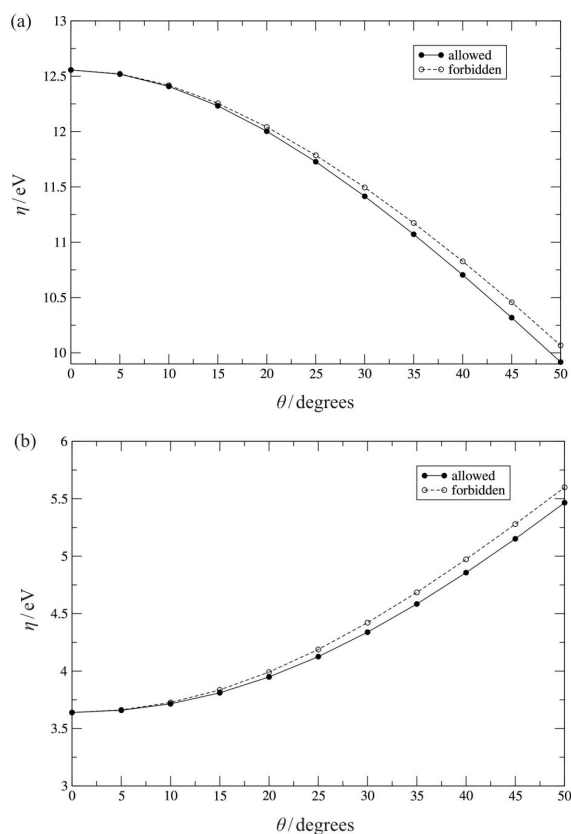
potential energy surface.

For the molecules under study, a sigmatropic hydrogen shift essentially involves the transfer of a hydrogen atom from the terminal  $sp^3$  carbon atom to the terminal  $sp^2$  one. As explained in the previous section, this shift can be done in either of two modes: suprafacial or antarafacial. It is easily seen that a suprafacial shift, where the hydrogen atom stays at the same side of the carbon skeleton, is equivalent to a disrotatory movement of the terminal groups, whereas the antarafacial mode, for which the hydrogen has to cross the carbon plane, corresponds to a conrotatory displacement. This observation suggests a natural choice for the model reaction coordinate as the dihedral angle  $\theta$  between a hydrogen atom on the terminal  $sp^2$  carbon and the planar carbon skeleton. This angle quantifies the conrotatory or disrotatory movement depending on the sense of the simultaneous twist of the terminal  $-CH_3$  group.

Since the idea is to predict the allowed reaction mode on the basis of the hardness response at the initial stage of the reaction, a variation of  $\theta$  from  $0^\circ$  to  $50^\circ$  is expected to be sufficient for capturing all the necessary information. The corresponding variations of the dihedral angle of the  $-CH_3$  hydrogen with the carbon plane are from  $0^\circ$  to  $\pm 33.3^\circ$  (depending on whether the suprafacial or antarafacial mode is considered). The difference in the range of the two angles is justified by the local symmetry of the groups.

For each molecule the initial hardness response is calculated for the thermal and photochemical reactions through both the suprafacial and antarafacial pathways. The thermal or ground state reaction corresponds to the situation where the molecules are in their singlet state, whereas the triplet state reaction is used as a model for the photochemical process. All results are visualised in Figures 3 to 6. The initial hardness response can be seen as a measure of the activation hardness, defined by Zhou and Parr as the difference between the hardnesses of the reactants and the transition state.<sup>41</sup> Based on the maximum hardness principle, smaller values of the activation hardness can be associated with more stable transition states and thus with faster reactions. So, the initial hardness response is expected to be related to the aromaticity concept in the case of pericyclic reactions, where the aromaticity governs the stability of the transition states which can either be aromatic or anti-aromatic depending on the reaction mode.<sup>17</sup>

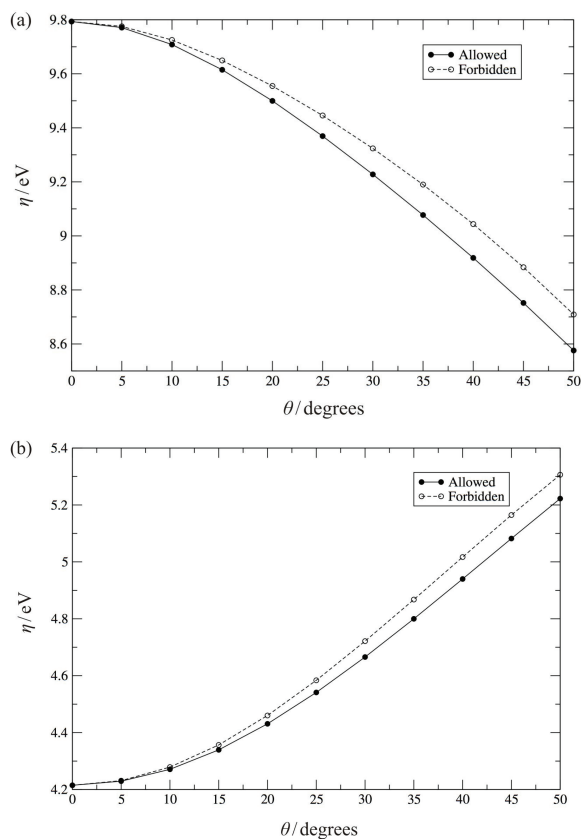
Generally, the results are convincing for 1,3-pentadiene and the 1,3-hexadiene cation. Figures 5a and 6a show the initial hardness along the singlet reaction paths. In both cases the highest values can be associated to the suprafacial mode, which indicates a higher activation hardness and thus a more aromatic and stable



**Figure 3.** (a) Model reaction coordinate for [1,3] H shift in propene in the singlet state (allowed (antarafacial) and forbidden (suprafacial) modes). (b) Model reaction coordinate for [1,3] H shift in propene in the triplet state (allowed (suprafacial) and forbidden (antarafacial) modes).

transition state. The triplet paths (Figures 5b and 6b) possess the inverse trend with the highest initial hardness response for the antarafacial mode, which is consequently predicted to be the preferred case. These results are in perfect agreement with the Woodward-Hoffmann rules.

The propene and butene cation profiles in Figures 3 and 4, on the other hand, give an image opposite to what the Woodward-Hoffmann rules predict, which could at first sight be ascribed to a failure of the predictive properties of the initial hardness response. The correct interpretation should however be nuanced and two reasons could explain this apparent shortcoming. The Woodward-Hoffmann rules state that for the thermal reaction the [1,3] hydrogen shift in a neutral molecule and the [1,4] in a cation should proceed in an antarafacial way and the inverse for the photochemical reaction. It has however been observed that these rules can be violated on geometric grounds for small systems.<sup>42</sup> The molecular framework does not always permit an antarafacial shift to occur so that the transition state for the Woodward-Hoffmann forbidden reaction (the su-

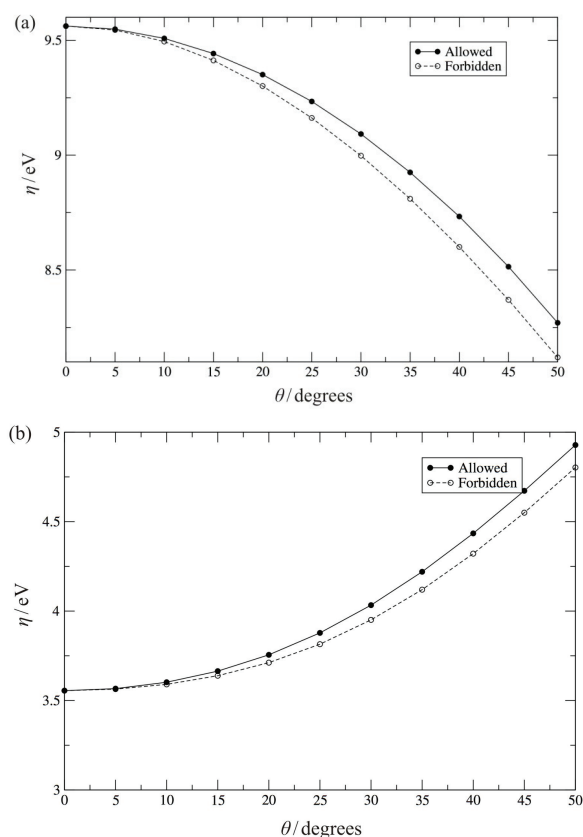


**Figure 4.** (a) Model reaction coordinate for the [1,4] H shift in the butene cation in the singlet state (allowed (antarafacial) and forbidden (suprafacial) modes). (b) Model reaction coordinate for the [1,4] H shift in the butene cation in the triplet state (allowed (suprafacial) and forbidden (antarafacial) modes).

prafacial one in the singlet case) could become lower in energy than the one for the Woodward-Hoffmann allowed process (the antarafacial one in the singlet case). This observation indicates that steric effects can obscure the strict utilisation of the rules.

A second possible factor could arise from the fact that the initial hardness response is calculated along a model reaction path. For propene and butene, small molecules with a limited conformational freedom, our choice of reaction coordinate could be quite deviating from the real one. The calculated hardness profiles are consequently not representing the genuine process and could be erroneous. In order to check this hypothesis, intrinsic reaction coordinate<sup>43-44</sup> (IRC) paths were calculated for the sigmatropic hydrogen shifts in propene and the butene cation in their singlet states.

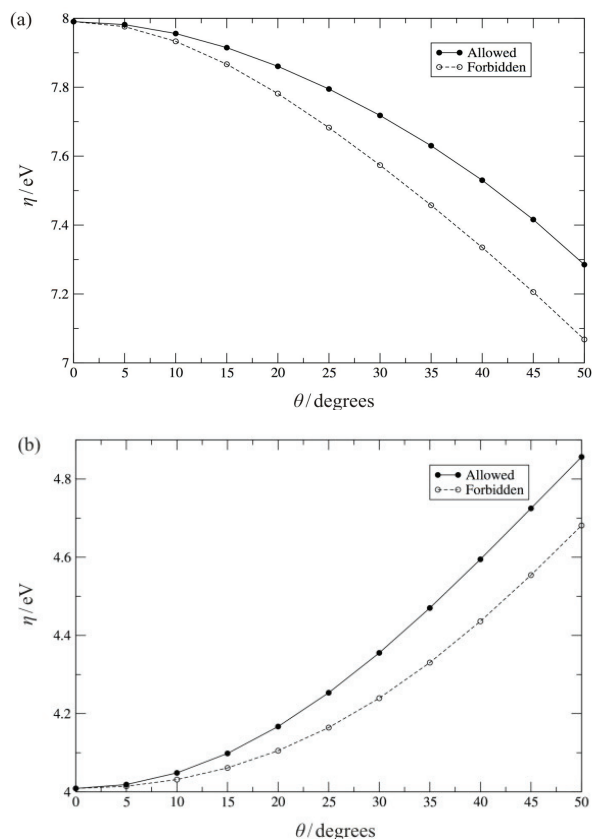
Figures 7 and 8 show the IRC energy and hardness profiles of the respective molecules. The IRC plots of propene give a twofold image. It seems that the activation energy of the suprafacial mode is lower than the antarafacial one, a result that is in agreement with the initial hardness response of our model reaction path



**Figure 5.** (a) Model reaction coordinate for the [1,5] H shift in pentadiene in the singlet state (allowed (suprafacial) and forbidden (antarafacial) modes). (b) Model reaction coordinate for the [1,5] H shift in pentadiene in the triplet state (allowed (antarafacial) and forbidden (suprafacial) modes).

(Figure 3a), but stands in contrast to the Woodward-Hoffmann rules. The deviation from the rules is plausible because of the aforementioned effect of steric hindrance. The IRC hardness profile, however, shows activation hardnesses which reproduce the Woodward-Hoffmann rules and describes the antarafacial mode to be preferred. The contradicting trend between the IRC activation energy and activation hardness is quite remarkable. It has however been discussed<sup>45,46</sup> that the activation hardness can give a correct description in cases where the energy fails due to an insufficient accuracy of the level of theory considered. The difference between the conclusions based on the initial hardness response and the transition state hardness is due to the specific behaviour of the IRC profiles (crossing close to the transition state) and is, as far as we tested, a unique case.

The IRC results for the singlet state of the butene cation in Figure 8 show that the activation energies, the activation hardnesses and the initial hardness responses for the genuine reaction paths are in accordance with the Woodward-Hoffmann rules. The hardness profile



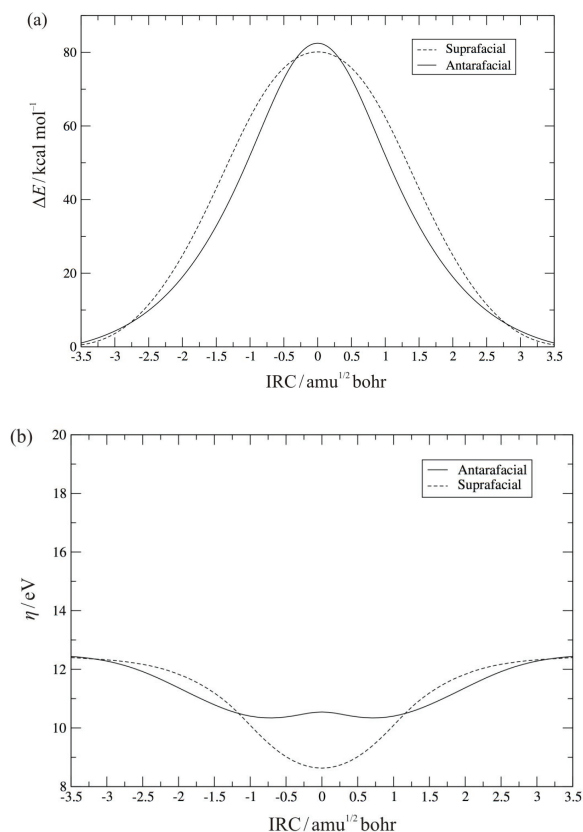
**Figure 6.** (a) Model reaction coordinate for the [1,6] H shift in hexadiene cation in the singlet state (allowed (suprafacial) and forbidden (antarafacial) modes). (b) Model reaction coordinate for the [1,6] H shift in hexadiene cation in the triplet state (allowed (antarafacial) and forbidden (suprafacial) modes).

proves that the initial response is an adequate tool for predicting the outcome of sigmatropic hydrogen shifts in this case as well. Care should however be taken that the chosen model reaction path sufficiently resembles the real one, a requirement that was apparently not fulfilled in our previous model.

## CONCLUSION

This paper is part of a series in which we aimed to cast the Woodward-Hoffmann rules into a conceptual DFT framework. After the cycloaddition and electrocyclisation reactions, the sigmatropic rearrangements are tackled in this contribution.

The general philosophy has always been to examine some relevant reactions of each class with typical DFT reactivity or stability indices, which showed that the use of the initial hardness response correctly predicts the preferred reaction modes. The observation that the initial hardness response can be linked to the activation hardness and associated aromaticity of the transition

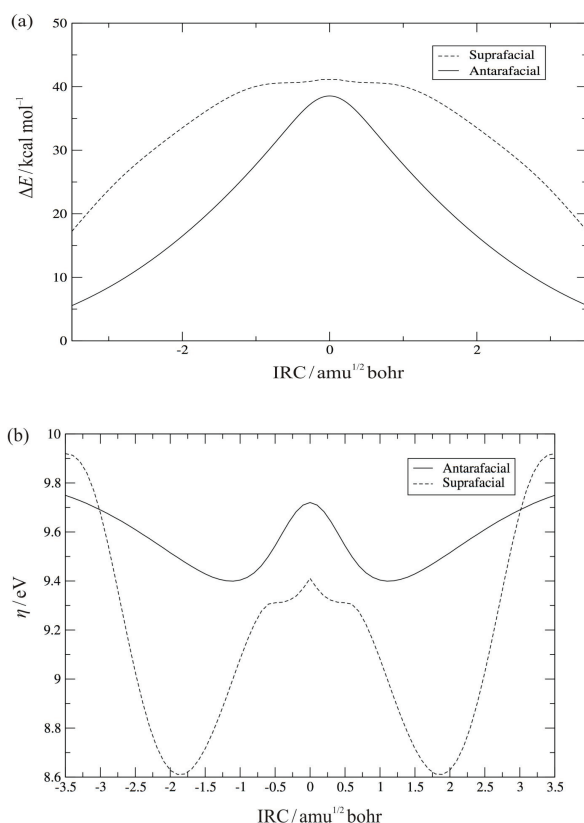


**Figure 7.** (a) Antarafacial and suprafacial IRC energy paths of the [1,3] H shift in propene in the ground state. (b) Antarafacial and suprafacial IRC hardness profiles of the [1,3] H shift in propene in the ground state.

state is a clear justification of the connection of this concept with the Woodward-Hoffmann rules. We argued that it is not strictly obligatory to know the real reaction path, but that the hardness response along a well-chosen model path contains all the necessary information.

With regard to the sigmatropic rearrangements, we showed that the choice of an adequate model reaction coordinate can easily be done for molecules consisting of five or more carbon atoms. For the smaller systems, it seemed very important to ascertain that the model reaction coordinate closely resembles the genuine one in order to reflect the correct situation. Generally, we proved that the Woodward-Hoffmann rules can be recovered by the initial hardness response for this reaction class, in line with previous results for electrocyclisations and cycloadditions.

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**Figure 8.** (a) Antarafacial and suprafacial IRC energy paths of the [1,4] H shift in the butene cation in the ground state. (b) Antarafacial and suprafacial IRC hardness profiles of the [1,4] H shift in the butene cation in the ground state.

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**SAŽETAK****Redefinicija Woodward-Hoffman-ovih pravila u kontekstu konceptualne DFT teorije: slučaj sigmatropnih reakcija****Nick Sablon, Frank de Proft i Paul Geerlings***Eenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB), Faculteit Wetenschappen, Pleinlaan 2, B-1050 Brussels, Belgium*

U ovom je radu proučavana mogućnost primjene inicijalne tvrdoće, indeksa reaktivnosti unutar konceptualne DFT teorije, u predviđanju dozvoljenog ili zabranjenog karaktera serije reakcija sigmatropnih pomaka vodika, koji se tradicionalno objašnjavaju pomoću poznatih Woodward-Hoffman-ovih pravila za pericikličke reakcije. U prethodnim radovima, primijećeno je da ta veličina može biti povezana s aktivacijskom tvrdoćom kemijske reakcije, te stoga i s aromatičnošću prijelaznog stanja u tom tipu kemijskih reakcija. Pokazano je, uzimajući u obzir i aproksimativnu reakcijsku koordinatu i prirodenu reakcijsku koordinatu da dozvoljeni način sigmatropne pregradnje odgovara najvećoj vrijednosti inicijalne tvrdoće u skladu s prijašnjim radovima o reakcijama cikloadicije i elektro-ciklizacije.