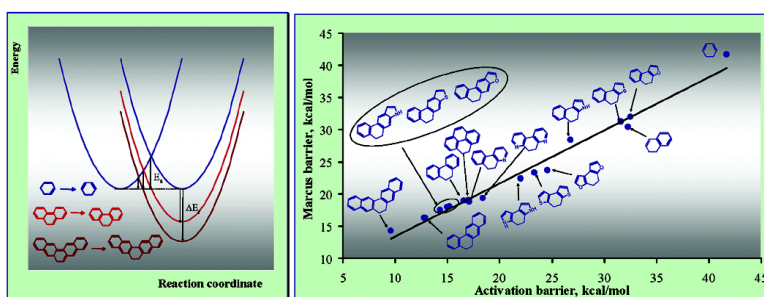


Control of Kinetics and Thermodynamics of [1,5]-Shifts by Aromaticity: A View through the Prism of Marcus Theory

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Control of Kinetics and Thermodynamics of [1,5]-Shifts by Aromaticity: A View through the Prism of Marcus Theory

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Abstract: The effects of aromatic stabilization on the rates of [1,5]-hydrogen shifts in a series of carbo- and heterocyclic dihydroaromatic compounds were estimated by B3LYP/6-31G** computations. The aromatic stabilization energy of the product is directly translated into increased exothermicity of these reactions. Relative trends for a significant range of endothermic and exothermic [1,5]-shifts with different intrinsic activation energies are reliably described by Marcus theory. The effects of aromaticity or antiaromaticity are very large and can lead to dramatic acceleration or deceleration of [1,5]-hydrogen shifts and even to complete disappearance of the reaction barrier. Not only the activation energy but the shape and position of the reaction barrier can be efficiently controlled by changes in the aromaticity of the products, making these systems interesting models for studying hydrogen tunneling. Marcus theory can also be applied successfully to other pericyclic shifts such as [1,5]-shifts which involve chlorine and methyl transfer.

Introduction

The [1,5]-sigmatropic hydrogen shift (Figure 1) is a textbook pericyclic reaction^{1–3} which has stimulated many mechanistic studies^{4,5} and has found numerous applications in organic synthesis.^{6,7} Detailed discussions of [1,5]-shifts from different perspectives have recently been presented.^{8–11} After years of controversy, it is generally accepted that this reaction usually proceeds by a concerted pathway^{11–13} involving an aromatic transition state.¹⁴

The [1,5]-shifts in simple cyclic and acyclic compounds are relatively slow as a consequence of substantial activation energies.¹⁵ For example, the activation energy for the [1,5]-shift in 1,3-pentadiene is 36 kcal/mol and is even higher (41 kcal/mol) in 1,3-cyclohexadiene.⁹ Thus, we were intrigued by the results of a recent experimental study¹⁶ which found that

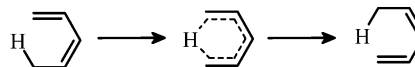


Figure 1. Parent [1,5]-hydrogen shift in (Z)-1,3-pentadiene.

the [1,5]-shift which transforms 8a,9-dihydrophenanthrene intermediate **2R** (produced by the “symmetry-enforced” photocyclization of α -phenyl-substituted 2-vinylbiphenyl shown in Scheme 1) into 9,10-dihydrophenanthrene **2P** proceeds rapidly even at low temperatures (100 K). It was pointed out that formation of two aromatic rings in the product, which leads to high exergonicity of the [1,5]-shift, is responsible for the observed lowering of the activation barrier. This is certainly a reasonable suggestion consistent with numerous “aromaticity-driven” processes scattered throughout chemical literature.^{17,18} However, only a single example of a similar accelerating effect in a [1,5]-shift has been reported – the transformation of isoidene **3R** to indene **3P** (Scheme 1).^{4a,19} There is no

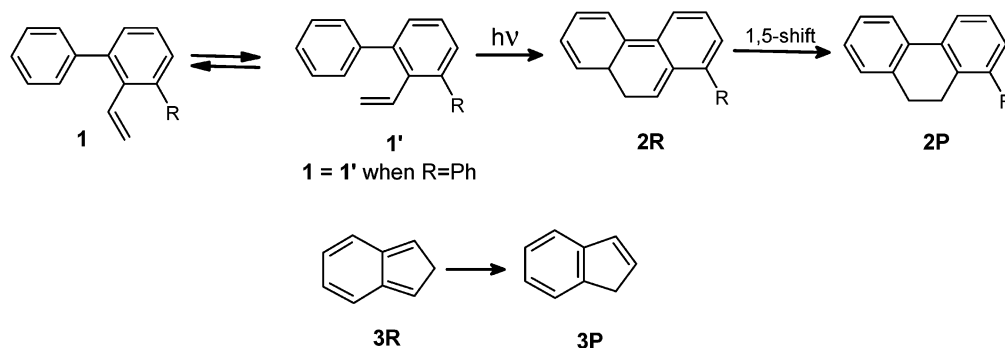
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Scheme 1. “Symmetry-Enforced Cyclization” of Vinyl Biphenyl **1** Followed by [1,5]-Hydrogen Shift in 8a,10-Dihydrophenanthrene **2R** To Give 9,10-Dihydrophenanthrene **2P** (R Stands for Reactant, P Stands for Product) (Top); Isoindene–Indene Isomerization (Bottom)



information in the literature which indicates to what extent aromatic stabilization is translated into a decrease in the activation energy for a [1,5]-shift.

The goals of this study were two-fold. We wanted to both explain the experimental results for the reactions shown in Scheme 1 and determine the general relation between the exothermicity and activation energy of [1,5]-shifts. In particular, we were interested in determining to what extent the increase in aromatic stabilization of the products changes the activation barrier and whether Marcus theory,²⁰ which can separate the thermodynamic and intrinsic contributions to the activation barrier,²¹ is capable of predicting these changes. Although Marcus theory was originally developed for electron-transfer reactions, it has been successfully applied to a wide variety of organic reactions,^{20–23} including pericyclic²⁴ and hydrogen- and group-transfer²⁵ reactions.

Calculation Details

Computations on a series of [1,5]-hydrogen shift reactions (Table 1) were performed by B3LYP²⁶ density functional with 6-31G** basis set using Gaussian 98.²⁷ Activation energies calculated at this level are in good agreement with the experimental data^{51,8,9} for [1,5]-hydrogen shifts in cyclopentadiene, 1,3-cyclohexadiene, and isoindene (Figure 2). Natural charges were obtained by using the natural bond orbital (NBO) analysis of Weinhold and co-workers.²⁸

The magnetic effects of aromaticity were estimated by nucleus independent chemical shift (NICS)²⁹ GIAO³⁰-B3LYP/6-311+G**//

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Table 1. The Activation and Reaction Energies (kcal/mol) of Various [1,5]-Shifts (1–21) in Carbo- and Heterocyclic Systems Calculated at the B3LYP/6-31G** Level

No.	Reaction	$\Delta E_{\text{DFT}}^{\ddagger}$	$\Delta E_{\text{Marcus}}^{\ddagger}$ ^a	$\Delta E_{\text{ZPE}}^{\ddagger}$ ^b	$\Delta H_{298}^{\ddagger}$	$\Delta G_{298}^{\ddagger}$	ΔE_{rxn}	$\Lambda_{\text{p}}^{\text{c}}$
7		41.7	41.7	39.4	39.0	40.1	0.0	0.00
8a		32.3	30.4	29.5	29.1	29.9	-24.3	-14.87
8b		27.3	27.0	26.1	25.4	26.7	-32.6	-16.23
2		16.6	19.0	14.2	13.8	14.8	-54.2	-19.61
9		12.8	16.2	10.6	10.1	11.5	-62.7	-30.39
10		12.9	16.2	10.6	10.2	11.6	-62.7	-25.67
11		9.6	14.3	8.1	7.8	10.7	-69.3	-35.86
12		17.1	18.7	14.9	14.3	15.7	-55.0	-23.40
13		17.0	19.0	14.7	14.2	15.5	-53.5	-19.59
14		18.4	19.3	16.1	15.6	17.0	-52.4	-20.86
15		24.6	23.7	22.2	21.8	23.1	-41.1	-10.76
16		23.3	23.3	20.8	20.3	21.5	-42.2	-14.51
17		22.0	22.4	19.9	19.3	20.6	-44.5	-12.10
18		32.5	31.9	30.2	29.8	30.9	-20.8	-6.44
19		31.6	31.3	29.5	29.0	30.2	-22.4	-9.61
20		26.8	28.4	24.6	24.1	25.2	-29.1	-8.02
21		15.2	18.1	12.9	12.4	13.6	-57.0	-22.81
22		15.0	17.9	12.8	12.2	13.3	-57.5	-24.68
23		14.3	17.5	12.1	11.7	12.8	-58.7	-23.48
5		27.0	27.0	25.3	24.7	26.0	0.0	0.0
24		18.4	16.9	16.5	15.9	17.1	-22.5	-9.62
25		14.8	13.3	13.0	12.5	13.8	-32.1	-19.91
26		2.6	6.6	2.1	1.9	3.2	-54.5	-26.53

^a The activation barriers were calculated from Marcus theory (eq 1). ^b B3LYP activation energies + ZPE (zero point energy) corrections. ^c The magnetic susceptibility exaltation (MSE) of the product.

B3LYP/6-31G** calculations. The global aromaticity of the products was evaluated by the magnetic susceptibility exaltation (MSE or Λ_{p})³¹ calculated at the CSGT³²-B3LYP/6-31+G**//B3LYP/6-31G* level.

The effects of aromaticity on the transition state energies were analyzed using Marcus theory.²⁰ In Marcus theory, the energy of activation (ΔE^{\ddagger}) of a reaction is the sum of the intrinsic barrier and the thermodynamic contribution. The intrinsic barrier ($\Delta E_{\text{o}}^{\ddagger}$) represents the barrier of a thermoneutral process ($\Delta E_{\text{rxn}} = 0$). The thermodynamic contribution can be either positive or negative depending upon whether the reaction is endothermic or exothermic. The activation energy increases when $\Delta E_{\text{rxn}} > 0$ (an endothermic reaction) and decreases when

$\Delta E_{\text{rxn}} < 0$ (an exothermic reaction). When potential energy surfaces for the reactants and the products are approximated as parabolas, the Marcus barriers can be calculated from eq 1.

$$\Delta E^{\ddagger} = \Delta E_{\text{o}}^{\ddagger} + \frac{1}{2}\Delta E_{\text{rxn}} + \frac{(\Delta E_{\text{rxn}})^2}{16(\Delta E_{\text{o}}^{\ddagger})} \quad (1)$$

Results and Discussion

There have been several recent studies which thoroughly discussed [1,5]-shifts in prototype systems.^{5t,u,8,9} As a starting point in our analysis, we reproduced the theoretical results

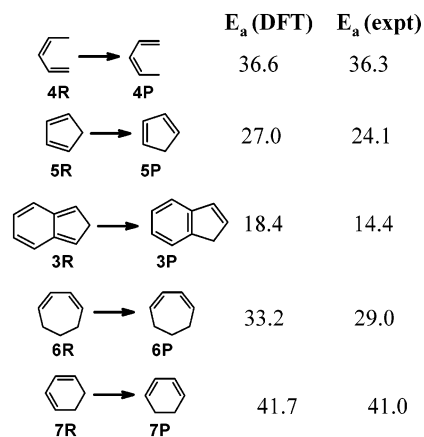


Figure 2. Comparison of the computed (B3LYP/6-31G**) and experimental activation energies (kcal mol⁻¹) of several [1,5]-hydrogen shifts.

reported in these studies, for example, for [1,5]-shifts in pentadiene, cyclopentadiene, and cyclohexadiene (Figure 2). The B3LYP functional gives reliable results for many pericyclic reactions.^{33,34} Whereas B3LYP somewhat overestimates the reaction barriers for [1,5]-shifts in five-membered and seven-membered rings, it succeeds in describing the relative trends for the [1,5]-shift in cyclopentadiene and isoidene. Moreover, the agreement between theory and experiment (Figure 2) is significantly better for [1,5]-shifts in six-membered rings which are the main class of compounds discussed in this paper.

Formation of aromatic rings in the products **2P** and **8P** renders the [1,5]-shifts in polyenes **2R** and **8R** highly exothermic (Figure 3). The magnitude of this effect depends on the number of newly formed benzene rings. The reaction is exothermic by 25 kcal/mol when dihydronaphthalene **8P**, containing one benzene ring, is formed. The energy release is larger (54 kcal/mol) in the case of 9,10-dihydrophenanthrene **2P** where a biphenyl π -system is

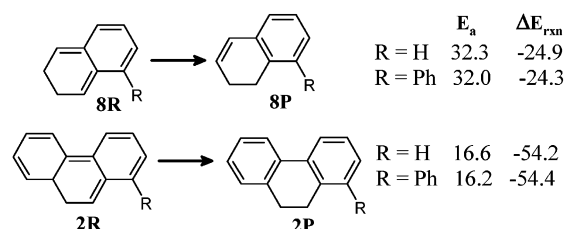


Figure 3. Activation and reaction energies (kcal mol⁻¹) of [1,5]-hydrogen shifts in polycyclic hydrocarbons with and without phenyl substitution calculated at the B3LYP/6-31G** level.

created. As a result, the activation energy for the [1,5]-hydrogen shift in 8a,9-dihydrophenanthrene **2R** is lowered to the extent that this reaction should be facile under ambient conditions.³⁵ Such large effects of aromaticity on the reaction and activation energies of [1,5]-shifts in dihydroaromatic systems allow one to study the response of the activation energy to changes in the reaction energies over a range of >100 kcal/mol. In the following section, we will discuss the general relationships which control [1,5]-shifts in extended series of carbo- and heterocyclic model compounds.

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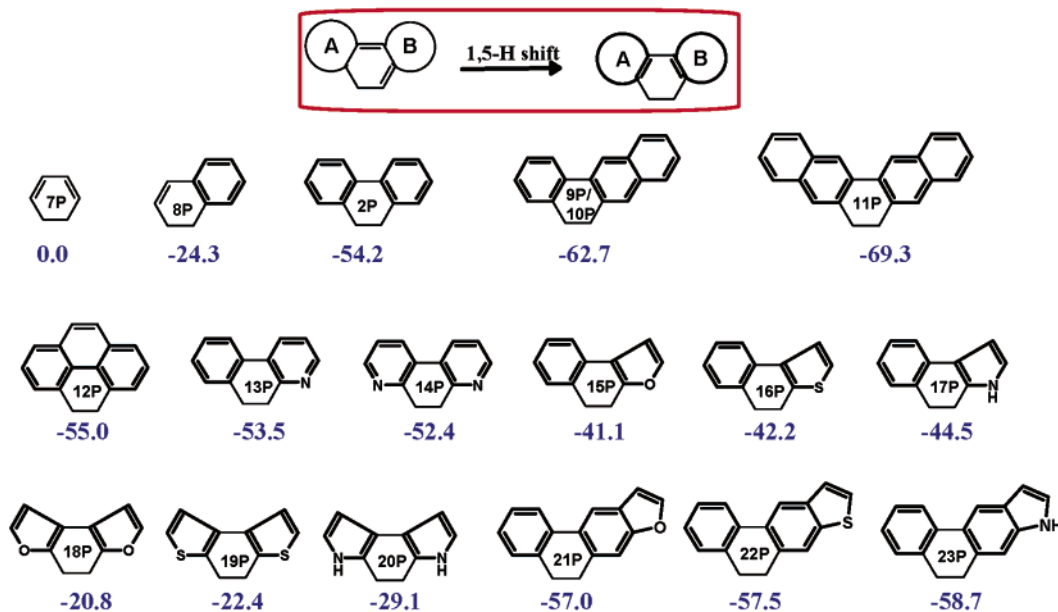


Figure 4. Exothermicity of the [1,5]-shift leading to formation of aromatic products. The newly formed aromatic systems are shown in bold.

Aromaticity: Effect of [1,5]-Shifts on Thermodynamics – Aromatic Stabilization Energies. The translocation of two double bonds during the [1,5]-shift may lead to the formation of up to two aromatic or heteroaromatic π -systems. The reaction energy directly reflects the gain in aromaticity associated with this exothermic process. The only caveat is that the computed reaction energies (ΔE_{rxn}) given in Figure 4 and in Table 1 cannot be taken directly as the aromatic stabilization energies for these systems because of the presence of several “cis–trans diene mismatches” discussed most recently by Schleyer and Puhlhofer.^{36,37}

When corrected for the “syn–anti mismatches”, the aromatic stabilization in the first benzene ring is worth 31.5 kcal/mol. The formation of biphenyl leads to an extra 32.8 kcal/mol increase in the aromatic stabilization. These numbers are in excellent agreement with recent estimates.³⁶ Thus, the relative reaction energies of the [1,5]-shifts in different carbo- and heterocyclic structures shown in Figure 4 can be taken as a measure of the relative aromaticity of the products.

As expected, the extra gain in aromatic stabilization progressively decreases when more extended aromatic moieties are formed. Formation of a naphthyl ring in **9P** and **10P** provides only 8.5 kcal/mol of extra stabilization as compared to formation of the benzene ring in **2P**. Interestingly, the degree of stabilization is independent of the relative positions of the benzene and naphthyl unit in the products **9P** and **10P**. Further extension of the aromatic core which leads to dibenzodihydrophenanthrene **11P** adds another 6.6 kcal/mol to the total aromatic stabilization and brings it down to almost 70 kcal/mol!

The different aromaticities of heterocyclic systems provide another way for controlling exothermicities of [1,5]-shifts in dihydroaromatic systems. According to the data in Table 1 and Figure 4, the relative aromaticities in the corresponding carbo- and heterocyclic rings (benzene > pyridine; pyrrole > thiophene > furan) follow the same trend as those in the prototype rings.^{29a,38}

Use of isomerization reactions to quantify aromaticity is by no means a new idea and has been described in the literature.^{36,38–41} The advantage of the set of model compounds described in this paper is that many of them are readily available through the efficient photochemical route described by Lewis and co-

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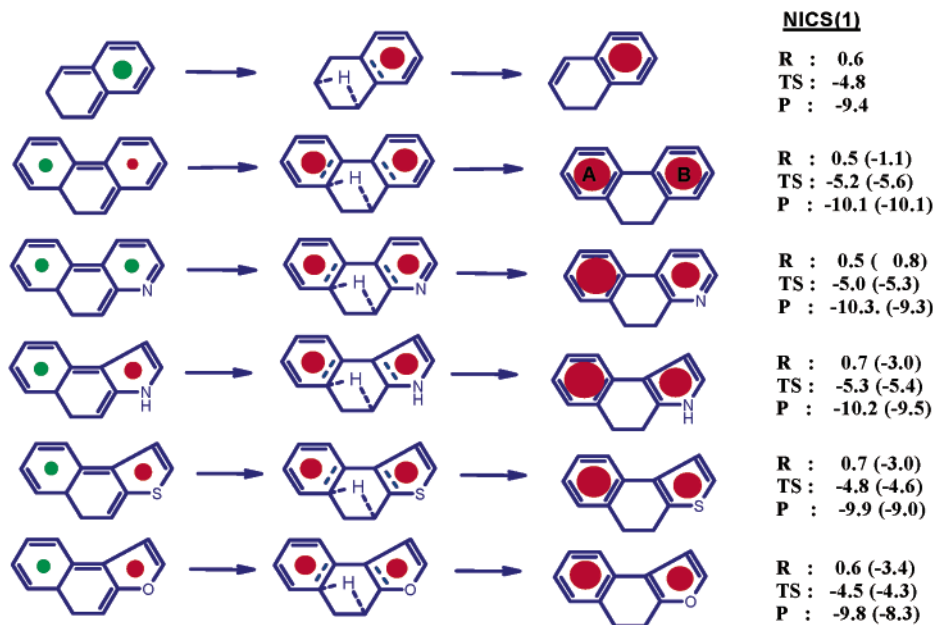


Figure 5. The illustration of aromatization in selected [1,5]-hydrogen shifts by NICS(1) values (B3LYP/6-311+G**/B3LYP/6-31G**) where the red and green circles denote the corresponding aromaticity and non- or antiaromaticity (the NICSs at “ring B” are given in parentheses).

workers (Scheme 1).¹⁶ Thus, the theoretical conclusions arrived at in this paper can be confirmed experimentally.

Aromaticity: Magnetic Criteria. The nuclear independent magnetic shift (NICS) method developed by Schleyer and co-workers²⁹ is a general and reliable magnetic criterion of local aromaticity (aromaticity at a given point in space). Aromaticity and antiaromaticity can be identified from the magnitude and sign of NICS values calculated at 1 Å above the ring center. The negative and positive NICS values correspondingly indicate diatropic and paratropic π -ring currents (aromaticity and antiaromaticity).

The NICS results show that six-membered side rings A and B are nonaromatic in the reactants but become progressively more aromatic in the transition states and the products (Figure

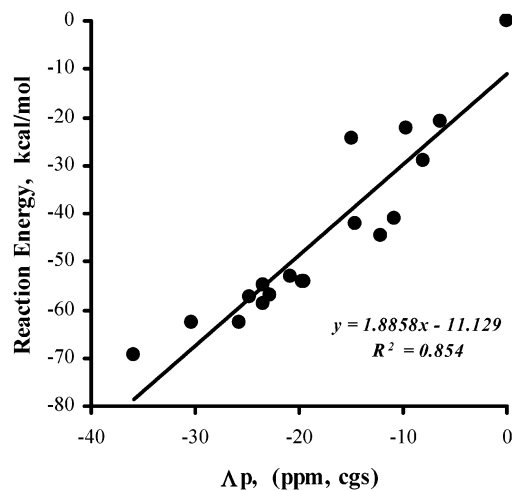


Figure 6. The correlations of the MSE of the [1,5]-shift products shown in Figure 4 (B3LYP/6-31+G**/B3LYP/6-31G*) with the reaction energies.

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5). In fact, the development of aromaticity in the product can be used as a reaction coordinate for such hydrogen shifts. Interestingly, the five-membered heterocyclic starting materials **15P–17P** are weakly aromatic, and the total gain of aromaticity in the products is smaller than that in their six-membered analogues. This observation is consistent with the lower exothermicities of the corresponding [1,5]-shifts.

The global aromaticity of the products can be estimated by magnetic susceptibility exaltation (MSE, Δ_p) calculations. The MSE is defined as the difference between the diamagnetic susceptibility (χ_M) of the cyclic conjugated system and that of a hypothetical ring with localized double bonds (χ_M').³⁹ For simplicity, the nonaromatic reactants were taken as the reference structures. NICS and MSE values are negative (diamagnetic) for aromatic compounds and positive (paramagnetic) for antiaromatic compounds. Figure 6 illustrates that the MSE values are in fact well correlated with the reaction energies and that both of these variables reflect the increased aromatic stabilization in the products. Thus, the magnetic properties are in accord with

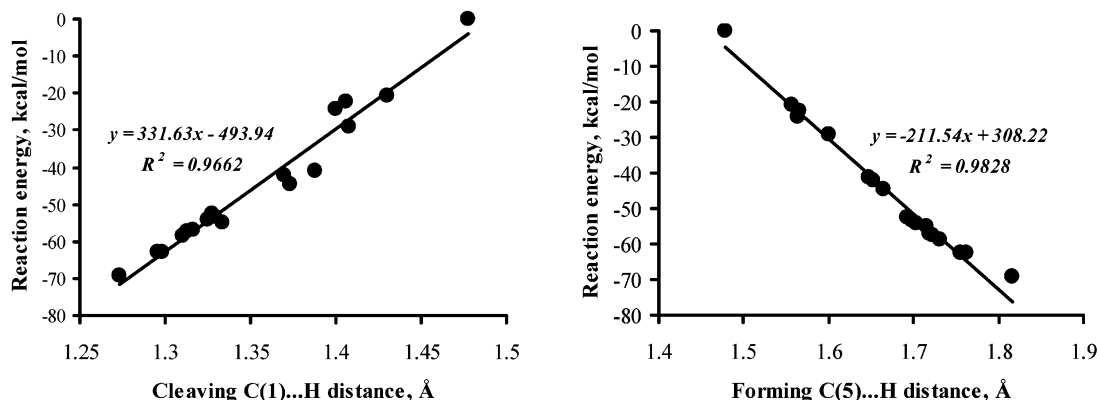


Figure 7. Correlations of the distances of cleaving and forming C \cdots H bonds at the TS with reaction energies (B3LYP/6-31G**) of the [1,5]-shift reactions in cyclohexadiene units (Table 1).

Table 2. The C–H Bond Distances (Å) and C1 \cdots H \cdots C5 Angles at the TSs of [1,5]-Hydrogen Shifts in Polycyclic Systems (B3LYP/6-31G** Computations)

no.	TS _{C1-H}	TS _{C5-H}	TS _{C1-H\cdotsC5}
7	1.478	1.478	98.8
8a	1.400	1.563	98.8
8b	1.398	1.601	98.0
2	1.325	1.703	98.4
9	1.298	1.755	96.4
10	1.296	1.762	95.4
11	1.273	1.817	95.0
12	1.334	1.715	93.8
13	1.329	1.698	96.8
14	1.328	1.692	96.4
15	1.388	1.648	98.1
16	1.370	1.652	97.8
17	1.373	1.664	97.2
18	1.430	1.557	96.9
19	1.406	1.565	98.0
20	1.408	1.601	96.9
21	1.316	1.719	96.1
22	1.313	1.723	96.1
23	1.310	1.731	95.8
5	1.312	1.312	69.3
24	1.245	1.405	68.2
25	1.224	1.450	67.1
26	1.181	1.588	63.3

the energetic effects of aromaticity described in the previous section. In the following section, we will discuss structural effects of aromaticity in these systems.

Aromaticity: Structural Criteria. The structural effects of aromaticity are most clearly displayed in the transition states (TS) for the reactions involving [1,5]-shifts. In accord with earlier findings,^{5t,u,8,9} all of these TSs are nonlinear. The migrating hydrogen moves along the trajectory with the C1HC5 angle in the range 93–99° at the TS (Table 2) where hydrogen can maintain continuous overlap with the π -system. Interestingly, the C1HC5 angles in the corresponding TS of pentadiene and cyclopentadiene are 133.7° and 69.3°, respectively.

Formation of the C1–C2 and C3–C4 π -bonds and the C5–H σ -bond is simultaneous with partial cleavage of the C2–C3 and C4–C5 π -bonds and the C1–H σ -bond at the TS. Transition states for exothermic [1,5]-shifts are “early”, reactant-like, and display shorter C1–H bonds and longer incipient C5 \cdots H bonds.⁴² Thus, all [1,5]-shifts in these systems are concerted but asynchronous. The early character of the transition states is

a direct consequence of the Leffler–Hammond postulate⁴³ and the Bell–Evans–Polanyi principle⁴⁴ – as the aromatic stabilization of the product increases and the reaction becomes more exothermic, an earlier TS is observed. As a result, there is an excellent correlation between the C1–H and C5–H distances at the TS (corresponding to cleaving and forming C \cdots H bonds) and reaction energies (Figure 7). It is interesting to note that the progressive shift of transition states to the “early” structures can also be described by relative changes in the π -bonds lengths which accompany the transformation from the bond alternating polyenes to the aromatic structures (Figure 8).⁴⁵ The observation of very narrow barriers and early transition states for highly exothermic [1,5]-shifts may have important practical implications because both of these factors should facilitate tunneling of the migrating hydrogen through the barrier⁴⁶ and can thus contribute to the very fast reaction rates observed by Lewis et al.¹⁶

The effect of aromatic stabilization of the products on reaction kinetics (Figure 9) can be readily understood from the Marcus theory analysis illustrated in Figure 10. The correlation of DFT barriers ($\Delta E_{\text{DFT}}^\ddagger$) with the Marcus barriers ($\Delta E_{\text{Marcus}}^\ddagger$) obtained by substituting DFT reaction energies in eq 1 is shown in Figure 11.⁴⁷ The range of activation energies (9–32 kcal/mol) and reaction energies (20–69 kcal/mol) is sufficiently large (Figure 11) for this correlation to possess considerable predictive power.⁴⁸

One practical consequence from the correlation of activation energies with aromaticity of reaction products is that reaction rates can be controlled by the nature of the product. For example, if preexponential factors are similar, formation of pyridines **13P**–**14P** should be 3–40 times slower than formation of **2P** because pyridine is less aromatic than benzene.^{29a,38b} Reactions yielding five-membered heteroaromatic rings **15P**–**20P** should proceed even more slowly. For example, the bisfuran **18P** should be formed 2 billion times more slowly than **2P**, and, thus, its precursor **18R** should be readily isolable under ambient conditions.

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(48) The correlations between DFT and Marcus activation enthalpies and free energies are equally good.

(42) Only TS for the degenerate [1,5]-shift in cyclohexadiene has C_s symmetry.

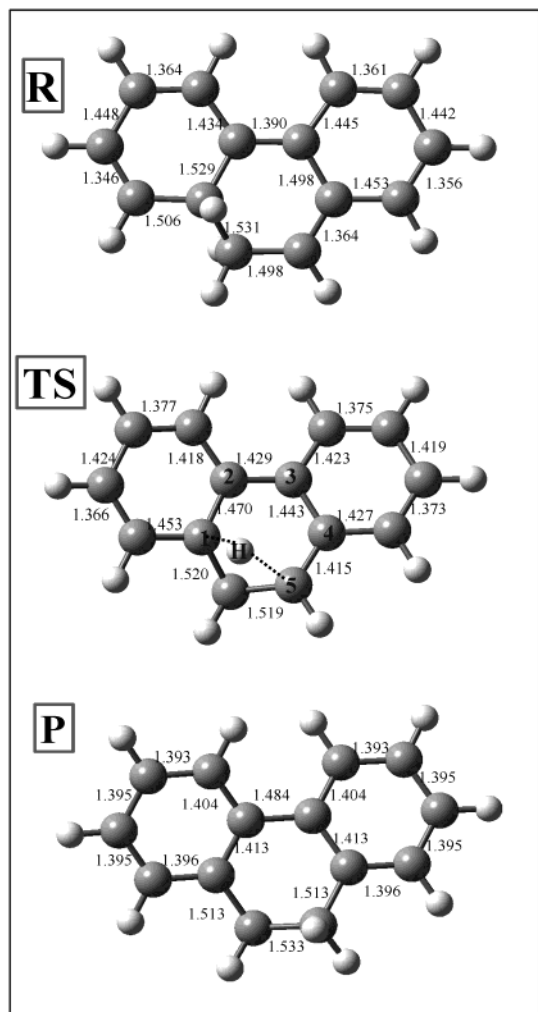


Figure 8. Changes in the bond lengths during the [1,5]-hydrogen shift in 9,10-dihydrophenanthrene **2** (B3LYP/6-31G**). Effect of aromaticity on reaction kinetics: Marcus theory treatment.

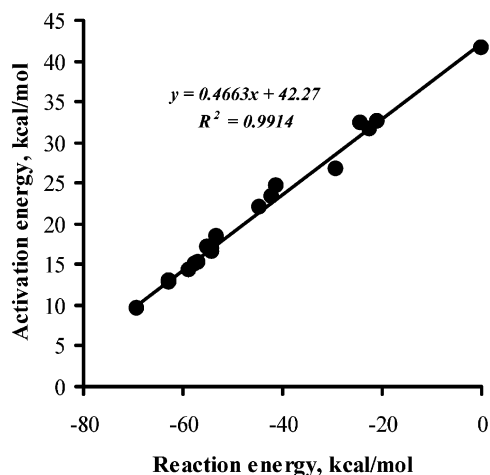


Figure 9. The correlations of the activation barriers versus reaction energies (B3LYP/6-31G**) of [1,5]-shift reactions in cyclohexadienyl-type dihydroaromatic compounds.

Marcus theory successfully disentangles the effect of the thermodynamic contribution to [1,5]-shifts kinetics in the cyclohexadiene series. The above correlation can be used for a semiquantitative estimate of activation energies once the exothermicities of these reactions are known. Because calculations

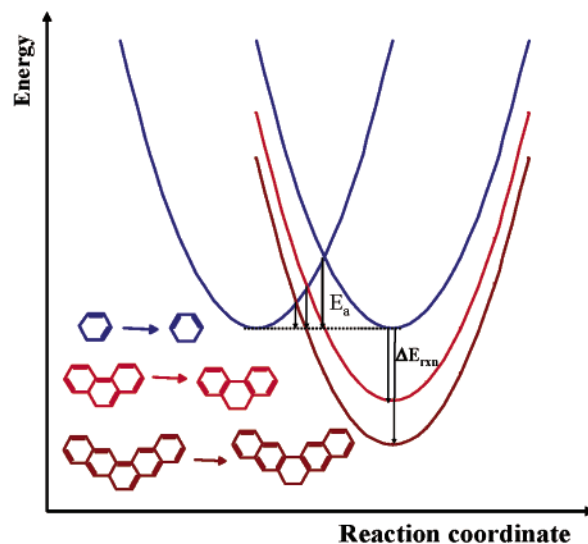


Figure 10. Marcus parabolae approximating potential energy curves for the degenerate and exothermic [1,5]-hydrogen shifts.

of reactions energies are significantly less expensive computationally than are computations of transition states, this finding has important practical implications for designing synthetic routes utilizing this pericyclic reaction or for other practical applications (vide infra).

Endothermic [1,5]-Hydrogen Shifts in Cyclohexadiene Systems and Antiaromatic Destabilization in the [1,5]-Hydrogen Shift. Not surprisingly, an equally good correlation between the reaction energy and reaction barrier (Figure 12) is found for highly endothermic [1,5]-shifts which transform aromatic starting materials **7P–23P** to nonaromatic products **7R–23R** (the reverse reactions of exothermic [1,5]-shifts discussed in the previous sections). Note, however, that the slope of the correlation between the DFT and Marcus barriers in Figure 12 is slightly larger than unity and the intercept is negative, whereas for the exothermic reactions in Figure 11 the slope is less than unity and the intercept is positive. We will analyze this in more detail at the end of this section.

We further extended this analysis to systems where [1,5]-hydrogen shifts lead to formation of antiaromatic cyclobutadiene moieties such as cyclohexadienes **27R** and **28R** (Figure 13). Even though the activation energies for these processes are extremely high and the reactions are highly endothermic, they are still well described by the Marcus equation (eq 1) and correspond well to the correlations given in Figures 11 and 12.

The data for both aromatic and antiaromatic (or nonaromatic) product formations can be combined in an excellent linear correlation shown in Figure 14. For comparison, this figure also provides the correlation of Marcus activation energies with reaction energies.⁴⁹ An interesting observation is that, although the Marcus curve follows the expected parabolic dependence, there is no need for the quadratic correction term for the perfectly linear correlation of DFT reaction and activation energies. The reasons for this somewhat surprising phenomenon are not clear. One could argue that the monoconfigurational B3LYP method can underestimate energies of reactants for highly exothermic shifts where the presence of low energy

(49) As was expected from the mathematics behind the Marcus theory, the correlation of the Marcus barriers with reaction energies is parabolic, and the R^2 value is exactly 1.

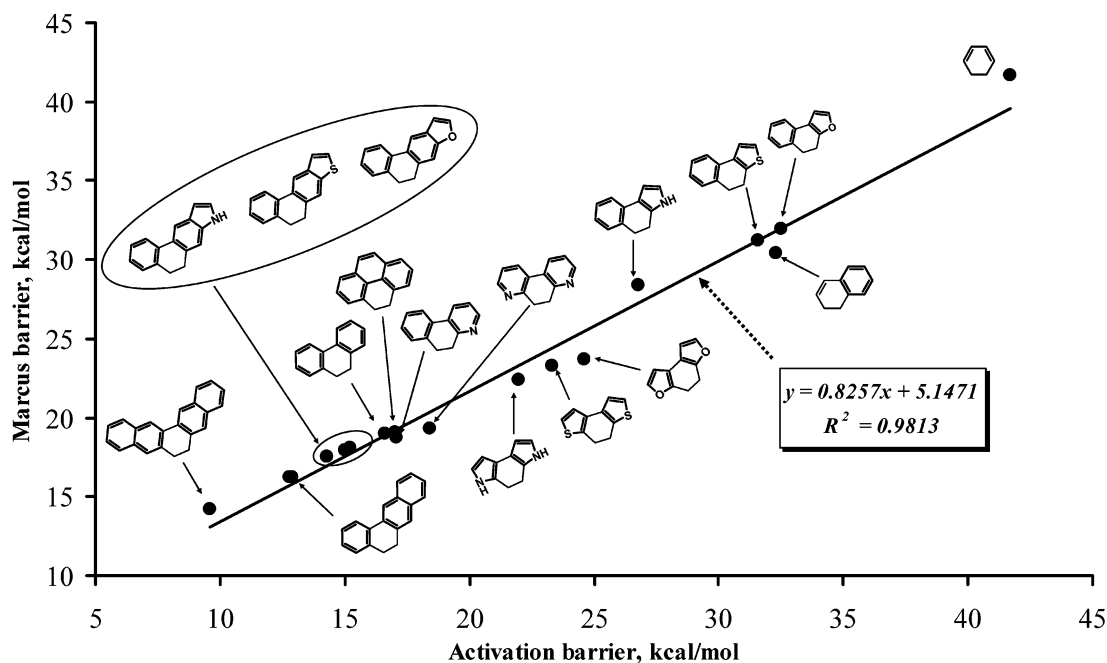


Figure 11. A correlation of calculated (B3LYP/6-31G**) activation barriers for exothermic [1,5]-hydrogen shift reactions (see Table 1) with the Marcus barrier.

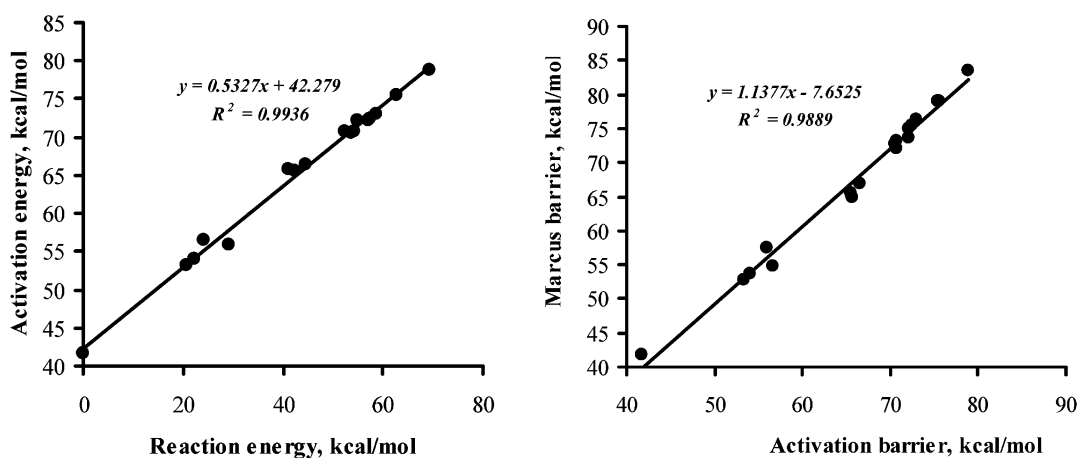


Figure 12. The correlations of the activation barriers for the *retro* [1,5]-hydrogen shifts (Table 1) versus Marcus barriers as well as reaction energies calculated at the B3LYP/6-31G** level.

excited states suggests the use of a multiconfigurational theoretical method for higher accuracy. However, this should not be a problem for the starting materials of highly endothermic shifts, which should be reasonably well described by DFT. It seems that a higher level multiconfigurational study is needed to understand whether the divergence between the two curves in Figure 14 is a spurious artifact of DFT or a real phenomenon of fundamental importance.

Changes in the Intrinsic Barrier. The previous sections establish the ability of Marcus theory to provide accurate descriptions of both exothermic and endothermic [1,5]-hydrogen shifts. To show the generality of this finding, we extended our analysis to other [1,5]-shifts with different intrinsic energies. The intrinsic energy can be changed (a) by changing the properties of the π -system, such as constraining it in a five-membered ring instead of a six-membered ring, or introducing a heteroatom bridge, and (b) by changing the nature of the migrating group (e.g., Me or Cl). Let us first analyze how a

change in the properties of the π -system is reflected in the intrinsic activation energy for the [1,5]-shift.

(A) [1,5]-Hydrogen Shifts in the Cyclopentadiene Series. [1,5]-Hydrogen shifts in cyclopentadiene proceed much faster than those in cyclohexadiene – the activation energy is 14 kcal/mol lower! A simple explanation for this effect is that in cyclohexadiene the termini of conjugated system are separated by a methylene group and their bridging through the migrating hydrogen increases the strain in the TS. In contrast, little or no increase in strain should accompany a [1,5]-shift in cyclopentadiene where the hydrogen atom migrates to the adjacent carbon. A less obvious effect which facilitates [1,5]-shifts in cyclopentadiene even compared to the shift in its acyclic analog⁵⁰ is a larger contribution of the charge-separated aromatic

(50) When comparing the experimentally observed reaction rates of hydrogen shifts in acyclic and cyclic molecules, one also has to bear in mind the more favorable entropic component of the reaction free energy for the cyclic cases.

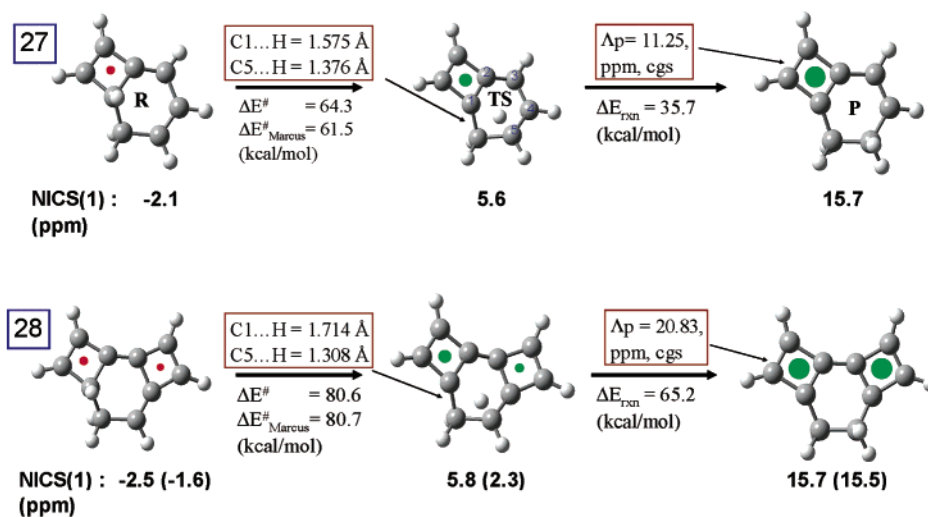


Figure 13. Computational analysis of [1,5]-hydrogen shifts leading to antiaromatic products **27P** and **28P** (B3LYP/6-31G**). The positive NICS(1) (B3LYP/6-311+G**/B3LYP/6-31G**) and MSE ($\Delta\rho_p$) of the product (B3LYP/6-31+G*/B3LYP/6-31G**) indicate the antiaromatic (green circles) behavior. The NICS values in parentheses are for the right side ring.

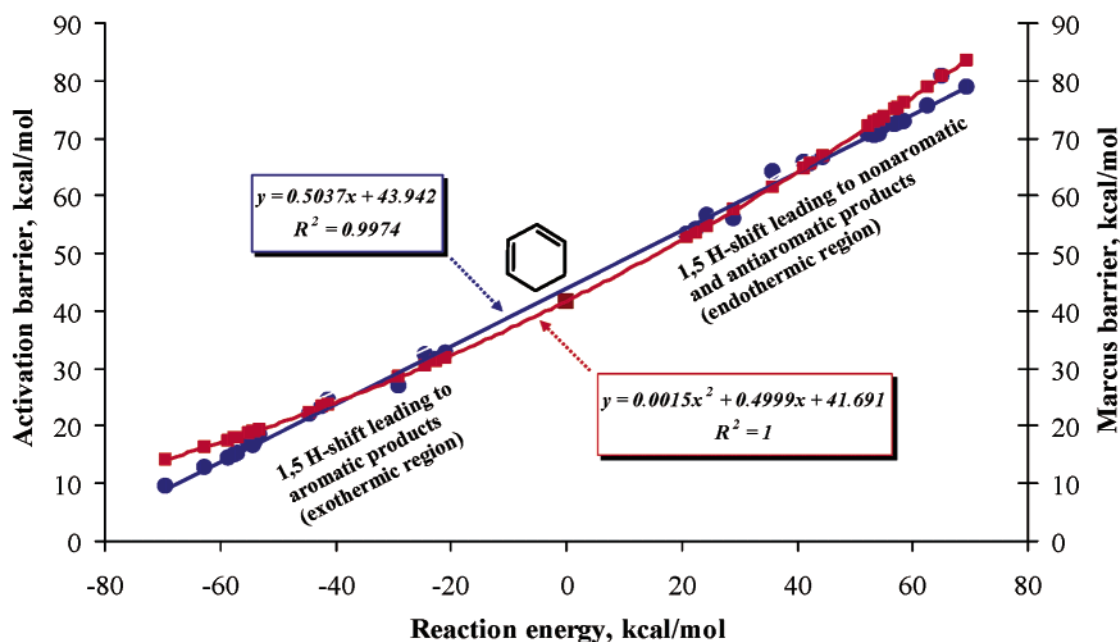


Figure 14. The general correlation of calculated (B3LYP/6-31G**) reaction energies with the activation barriers (blue circle) and the Marcus barriers (red square) for both exothermic and endothermic [1,5]-hydrogen shifts.

pentadienyl anion resonance structure, as illustrated in Figure 15.⁹ The increased contribution of this structure is reflected in more negative NICS(1) values and a significant increase in the positive charge at the migrating hydrogen for the TS in the case of cyclopentadiene systems.

Marcus analysis of [1,5]-shifts in cyclopentadienes was carried out in the same manner as above. The activation energy for the thermoneutral degenerate [1,5]-shift in cyclopentadiene was taken as the intrinsic activation barrier for these systems. The correlation between B3LYP and Marcus barriers is shown in Figure 16. For the first three members of the series (**5** and **24–26**), the correlation is remarkable ($R^2 = 0.999$). However, inclusion of the most exothermic [1,5]-shift, which yields fluorene, degrades the quality of the correlation ($R^2 = 0.953$). Although the correlation is still acceptable, it may point to a possible limitation of the Marcus approach for highly exothermic

reactions or a limitation of B3LYP in describing such highly asymmetric transition states (note similar deviations in analogous correlations for the cyclohexadiene series in Figures 11 and 14).⁵² Although B3LYP apparently overestimates the activation energies (Figure 2), the B3LYP reaction energy of ca. 20 kcal/mol is in perfect agreement with the experimental data of McCullough.¹⁹

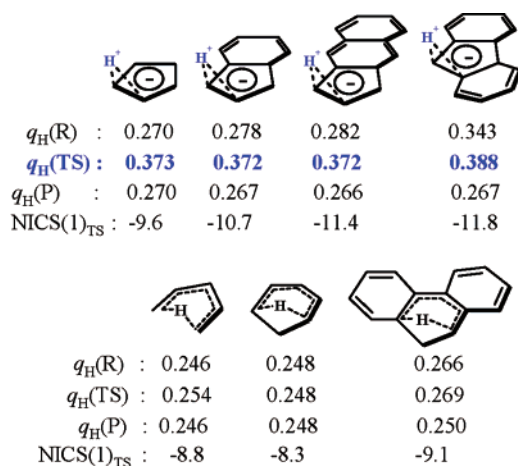
(B) [1,5]-Hydrogen Shifts in Heterocyclic Six-Membered Diens. The role of a bridge connecting two ends of the

- (51) Weinhold, F. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed. Wiley: New York, 1998; Vol. 3, p 1792. For more detailed earlier discussions, see: Foster, J. P.; Weinhold, F. F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. Reed, A. E.; Weinhold, F. F. *J. Chem. Phys.* **1983**, *78*, 4066. Reed, A. E.; Weinstock, F.; Weinhold, F. F. *J. Chem. Phys.* **1985**, *83*, 735. Reed, A. E.; Curtiss, L. A.; Weinhold, F. F. *Chem. Rev.* **1988**, *88*, 899.
- (52) The correlation between calculated and Marcus barriers for the 1,5-shifts in all cyclohexadienes and cyclopentadienes studied in this paper is given in the Supporting Information (Figure S4) and is also quite good.

Table 3. The Activation and Reaction Energies (kcal/mol) and Important TS Geometric Parameters for the [1,5]-Hydrogen Shifts (**29–34**) in Six-Membered Heterocycles Calculated at the B3LYP/6-31G** Level

No.	Reaction	$\Delta E_{\text{DFT}}^{\ddagger}$	ΔE_{rxn}	$\Delta E_{\text{Marcus}}^{\ddagger}$ ^a	TS _{C1..H}	TS _{C5..H}	TS _{C1..H..C5}
29		47.7	0.0	47.7	1.462	1.462	90.2
30		48.5	0.0	48.5	1.446	1.446	107.8
31		49.2	0.0	49.2	1.455	1.455	95.1
32		23.6	-49.4	26.2	1.325	1.663	88.3
33		23.0	-50.2	26.7	1.289	1.670	105.7
34		26.1	-44.3	29.5	1.310	1.673	92.8

^a The activation barriers were calculated from Marcus theory (eq 1).

**Figure 15.** Aromatic cyclopentadienyl anion contribution in the TSs of [1,5]-hydrogen shifts, natural (NBO)⁵¹ charges at the migrating hydrogen atoms, and NICS(1) computations at the center of the five-membered rings.

pentadienyl π -system was investigated by substituting the CH₂ group in cyclohexadiene with a heteroatom (O, N, or S) (Table 3). Introduction of these heteroatoms significantly increases the intrinsic activation energies for the hydrogen shifts in heterocyclohexadienes **29–31** [E_{a} (kcal/mol) = 41.7 (CH₂), 47.7 (O), 48.5 (S), 49.2 (NH)].⁵³ However, in all of these cases, the reaction and activation energies are nicely described by the Marcus equation (Figure 17).

(C) [1,5]-Chlorine and [1,5]-Methyl Shifts in 1,3-Cyclohexadiene Series. Another method for controlling the intrinsic energies for [1,5]-shifts is to change the migrating group. [1,5]-Methyl group shifts have much higher activation energies than topologically identical hydrogen shifts. For example, the activation energy of the degenerate methyl shift in 5-methyl-1,3-cyclohexadiene is 62 kcal/mol, ca. 20 kcal/mol higher than that for the analogous hydrogen shift (Figure 18). In contrast, activation energies for chlorine atom migrations are ca. 20 kcal/mol lower than those for the corresponding hydrogen shifts.⁵⁴ These differences, which allow for variation in the [1,5]-shift intrinsic activation energies by ca. 40 kcal/mol, are illustrated in Figure 18.

Correlations between the reaction energy and activation energy and between the Marcus barrier and calculated barrier

(53) The reaction barriers are in a good agreement with the extent of C1–H bond cleavage and C5 \cdots H formation at the TS as in the carbocyclic cases. Note, however, that C1..H \cdots C5 angles are very different in the heterocyclic system given in Table 3.

are shown in Figure 19. The slopes of these correlations are very similar and close to 0.5, as predicted by Marcus theory. This observation may point to a similarity in the underlying factors controlling all of these reactions. The most interesting consequence of the lower intrinsic energy of the [1,5]-chlorine shifts is that these reactions should become barrierless when their exothermicity reaches 45–50 kcal/mol. In fact, it is not possible to even optimize the geometry of the starting material **40R**, which is transformed to the product by the computer during the optimization process.

Practical Applications. (A) Control of the HOMO–LUMO Gap in Extended Polyunsaturated Systems. An interesting feature of [1,5]-shifts in extended dihydroaromatics is that these reactions transform a polyene into an aromatic compound. This change results in a large increase in the HOMO–LUMO gap within the product. The HOMO–LUMO gap (or band-gap in solid state physics) is directly related to various chemical, conducting, optical, and even mechanical properties,⁵⁶ including but not limited to chemical reactivity,⁵⁷ redox behavior,⁵⁸ elastic stiffness,⁵⁶ plastic flow resistance,⁵⁶ optical polarizability (refractive indices)⁵⁶ and nonlinear⁵⁹ properties, electric conductiv-

(54) This can be associated with the larger lengths of C–Cl bonds which make it easier to maintain continuous overlap with the migrating group in the TS.

(55) In theory, the slopes should be equal to 0.5, but in Figure 19 they are close to but not exactly equal to 0.5. In this case, one cannot be sure that this difference is statistically meaningful.

(56) Chemical, physical, and optical “hardness” as a function of the HOMO–LUMO gap: Gilman, J. J. *Mater. Res. Innovations* **1997**, *1*, 71.

(57) For a recent review with comprehensive analysis of the HOMO–LUMO gap and absolute and relative hardness in aromatic compounds, see: De Proft, F.; Geerlings, P. *Chem. Rev.* **2001**, *101*, 1451. See also: Haddon, R. C.; Fukunaga, T. *Tetrahedron Lett.* **1980**, *21*, 1191. Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722. Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron* **1985**, *41*, 785. Absolute hardness and relative hardness: Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371. Chemical hardness and Pauling scale of electronegativity: Komorowski, L. *Chem. Phys.* **1987**, *114*, 55. Komorowski, L. In *Chemical Hardness (Structure and Bonding, Vol. 80)*; Sen, K. D., Ed.; Springer-Verlag: Berlin, Heidelberg, 1993; p 45. Polycyclic hydrocarbons: Sinanoglu, O. *Int. J. Quantum Chem. Symp.* **1988**, *22*, 143. Sinanoglu, O. *Tetrahedron Lett.* **1988**, 889. Cioslowski, J.; Polansky, O. E. *Theor. Chim. Acta* **1988**, *74*, 55. Kekulene and antikekulene: Babic, D.; Trinajstić, N. *J. Mol. Struct. (THEOCHEM)* **1994**, *120*, 321. “Superbenzene”: Cioslowski, J.; O’Conner, P. B.; Fleischmann, E. D. *J. Am. Chem. Soc.* **1991**, *113*, 1086. Nonbenzenoid polycyclic aromatics: Bird, C. W. *Tetrahedron* **1998**, *54*, 10179 and references therein. Five-membered heteroaromatic compounds: Bean, G. J. *Org. Chem.* **1998**, *63*, 2497. Aromatic carbonyl compounds: Roy, R. K.; Choho, K.; De Proft, F.; Geerlings, P. *J. Phys. Org. Chem.* **1999**, *12*, 503. Derivatives of molecular valence as a measure of aromaticity: Balawender, R.; Komorowski, L.; De Proft, F.; Geerlings, P. *J. Phys. Chem. A* **1998**, *102*, 9912. Magnetic properties of large polybenzenoid hydrocarbons. Moran, D.; Stahl, F.; Bettinger, H. F.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 6746. The influence of the topology on the HOMO–LUMO energy gap in polyacenes. Andre, J.-M.; Champagne, B.; Perpete, E. A.; Guillaume, M. *Int. J. Quantum Chem.* **2001**, *84*, 607.

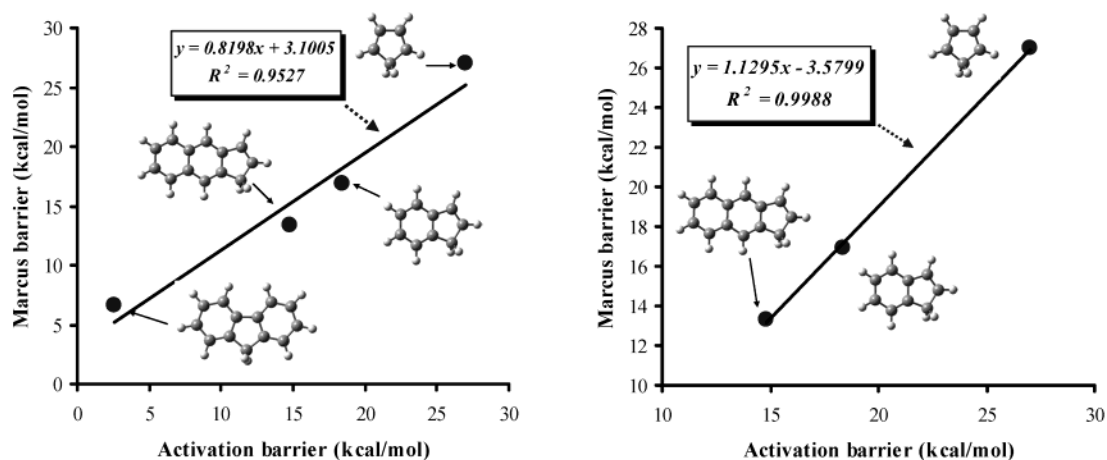


Figure 16. A correlation of the calculated (B3LYP/6-31G**) activation barriers of the [1,5]-hydrogen shift in various cyclopentadiene rings (5 and 24–26) with Marcus barriers.

Table 4. Changes in HOMO–LUMO Gaps (eV) as a Result of Selected [1,5]-Hydrogen Shifts (Wavelengths (in nm) for the Hypothetical Franck–Condon Photochemical Transitions with the Energy Corresponding Exactly to the HOMO–LUMO Gap Are Given in Brackets)

No.	Reaction	E(HOMO–LUMO) _R ^a	E(HOMO–LUMO) _P ^b
7		5.05 [246] (UV)	5.05 [246] (UV)
8		3.17 [391] (violet)	5.05 [246] (UV)
2		2.46 [504] (green)	4.99 [249] (UV)
9		1.76 [705] (red)	4.37 [284] (UV)
10		1.77 [701] (red)	4.37 [284] (UV)
11		1.30 [954] (IR)	4.05 [306] (UV)
12		2.03 [611] (orange)	4.68 [265] (UV)

^a HOMO–LUMO gap in the nonaromatic reactants. ^b HOMO–LUMO gap in the aromatic products.

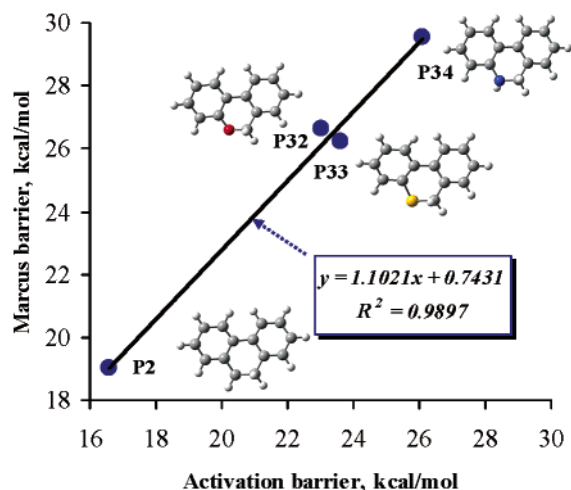


Figure 17. Correlation between activation and Marcus barriers (at the B3LYP/6-31G** level) of [1,5]-hydrogen shifts in compounds 2, 29–31.

ity,⁶⁰ optical absorption wavelength, etc. Table 4 illustrates how such changes in HOMO–LUMO gaps which accompany such [1,5]-shifts can lead to dramatic changes in the colors of materials which may incorporate such dihydroaromatic mol-

ecules. Such large effects are especially interesting because closely related molecules are promising building blocks for molecular electronic devices.⁶¹

(B) Ionization-Triggered Pericyclic Reactions. Changes in aromaticity due to ionization of reactants can be used for triggering [1,5]-shifts. The examples given in Table 5 illustrate how solvolysis of chloride **41R** under S_N2 conditions results in ca. 10¹⁰ acceleration of the [1,5]-shifts due to aromatic stabiliza-

(58) For a recent example of engineering the HOMO–LUMO gap in control of redox behavior, electron transfer, and spectroscopic properties, see: Perepichka, D. F.; Bryce, M. R.; Batsanov, A. S.; McInnes, E. J. L.; Zhao, J. P.; Farley, R. D. *Chem.-Eur. J.* **2002**, *8*, 4656.

(59) Nonlinear optical properties and the HOMO–LUMO gap of polyacenes. Lu, Y.-J.; Lee, S.-L. *Chem. Phys.* **1994**, *179*, 431.

(60) Effect of the HOMO–LUMO gap on conductance of organic molecules: Joachim, C.; Vinuesa, J. F. *Europhys. Lett.* **1996**, *33*, 635. Roitberg, A.; Mujica, V.; Ratner, M. A. 215th ACS National Meeting, Dallas, March 29–April 2, 1998. Kato, T.; Yamabe, T. *J. Chem. Phys.* **2003**, *118*, 3804. Yamaguchi, Y. *J. Chem. Phys.* **2003**, *117*, 9688. Kubiak, C. P.; Kasibhatla, B. S. T. 221st ANYL-180, Abstracts of Papers – American Chemical Society, 2001. Effect of location of the HOMO and LUMO levels with respect to the Fermi level of the metal electrode on conducting properties of molecular wires: Bredas, J. L.; Geskin, V. M.; dos Santos, D. A.; Beljonne, D.; Cornil, J. *Appl. Sci.* **1997**, *341*, 47. HOMO–LUMO gap as a structural element in the design of molecular metals. Kobayashi, A.; Suzuki, W.; Fujiwara, E.; Tanaka, H.; Okano, Y.; Kobayashi, H. *Synth. Met.* **2003**, *133–134*, 393. Kobayashi, A.; Tanaka, H.; Kobayashi, H. *J. Mater. Chem.* **2001**, *11*, 2078. For an example of a practical application in design of conducting copolymers, see: Wang, F.; Lai, Y.-H. *Macromolecules* **2003**, *36*, 536.

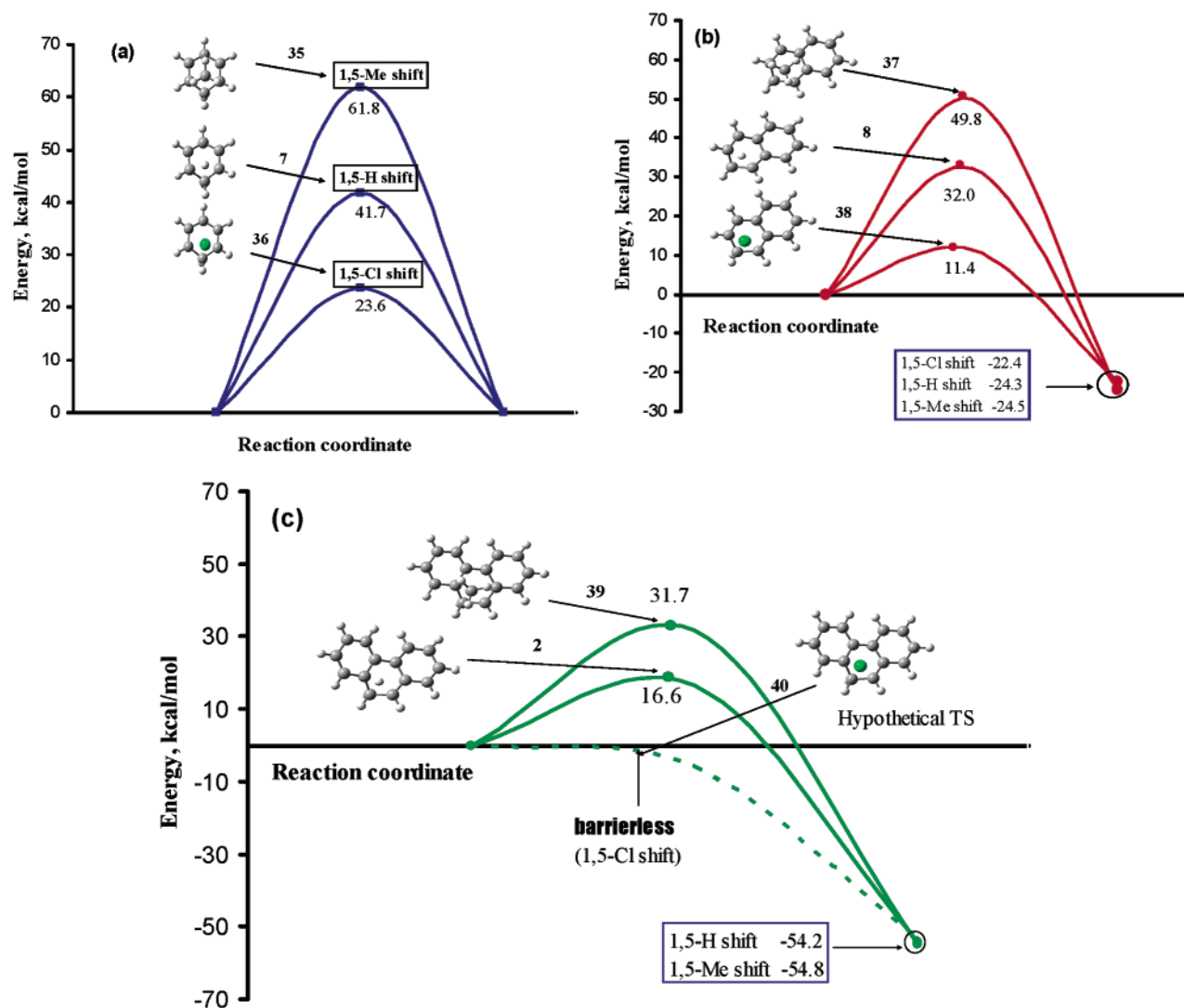


Figure 18. Comparison of the reaction pathways of [1,5]-hydrogen (a), [1,5]-methyl (b), and [1,5]-chlorine (c) shifts (B3LYP/6-31G** computations).

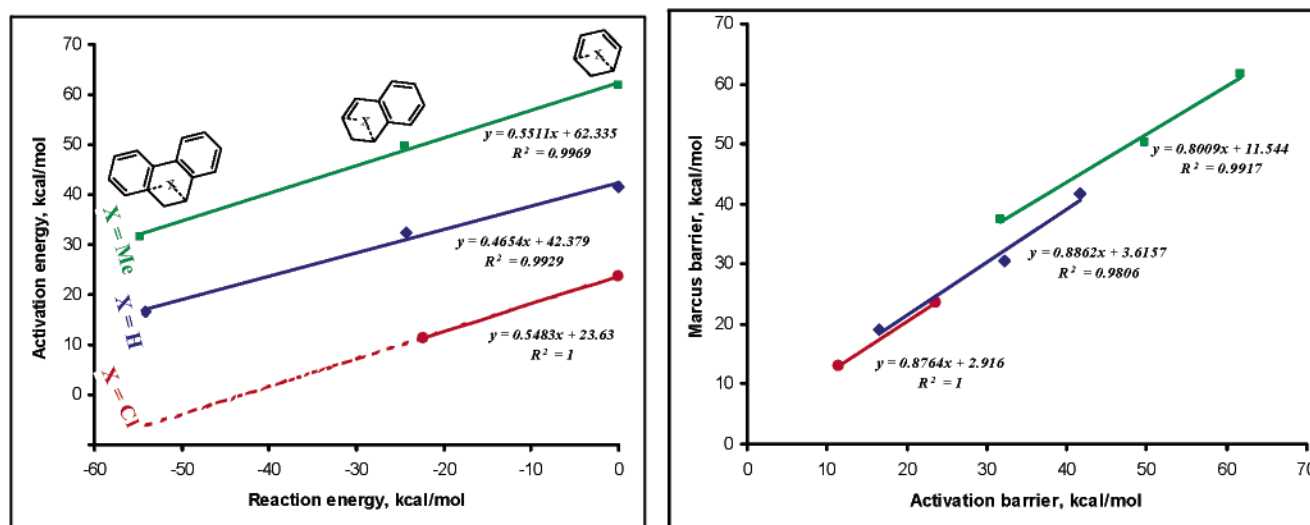
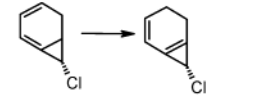
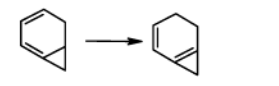
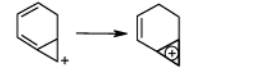
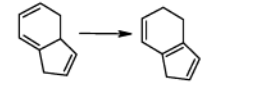
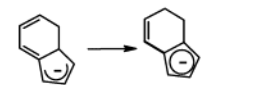
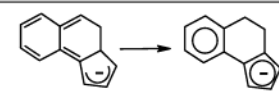


Figure 19. Comparison of [1,5]-hydrogen, [1,5]-methyl, and [1,5]-chlorine shift energies (B3LYP/6-31G** computations).⁵⁵

tion in cyclopropenyl cation **43P**. In a similar manner, deprotonation of dihydroindene **44R** or its analogues should result in a dramatic acceleration of the [1,5]-hydrogen shift leading

to the aromatic cyclopentadienyl anion products **45P** and **46P**. Such dramatic changes in reaction rates coupled with the abovementioned large changes in photophysical and conducting

Table 5. The Activation and Reaction Energies (kcal/mol) along with Selected TS Geometric Parameters for the [1,5]-Shifts Leading to Formation of Nonaromatic/Aromatic Cyclopentadienyl and Cyclopropenyl Derivatives (**41**–**46**) at the B3LYP/6-31G** Level (the NICS(1) Values (ppm) at the Cyclopentadiene and Cyclopropene Rings of the [1,5]-Shift Products Were Calculated at the B3LYP/6-311+G**//B3LYP/6-31G** Level)

No.	Reaction	$\Delta E_{\text{DFT}}^{\ddagger}$	ΔE_{rxn}	$\Delta E_{\text{Marcus}}^{\ddagger}$ ^a	$\text{TS}_{\text{Cl,H}}$	$\text{TS}_{\text{C5,H}}$	$\text{TS}_{\text{Cl,H,C5}}$	NICS(1) _p
41		51.7	7.3	45.4	1.440	1.482	95.4	-5.2
42		54.2	14.1	49.1	1.459	1.465	96.4	-4.3
43		37.9	-23.9	30.6	1.315	1.526	88.9	-12.1
44		39.4	-7.3	38.1	1.473	1.512	97.8	-2.0
45		27.1	-21.1	31.8	1.439	1.581	98.7	-8.8
46		22.7	-31.2	27.6	1.389	1.611	99.7	-6.7 (-6.8) ^b

^a The activation barriers were calculated from Marcus theory (eq 1). ^b The NICS value in parentheses for the six-membered aromatic ring.

properties which accompany these [1,5]-shifts may find interesting applications in the design of sensors and triggering devices in materials science.

Conclusion

Our computational study establishes that aromaticity is a key factor in controlling kinetics and thermodynamics of [1,5]-shifts. Reaction energies provide a direct method for quantifying aromaticity in the newly formed cyclic π -systems and controlling the activation energies of [1,5]-hydrogen, -methyl, and -chlorine shifts. Trends in the activation energies can be analyzed using Marcus theory. Interestingly, not only the height but also the shape and the position of the barrier can be efficiently

controlled, making these systems extremely interesting models for studies of hydrogen tunneling phenomena.

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Supporting Information Available: Figures showing the correlation between activation energy and cleaving/forming C–H bond, the activation and reaction energies of the *retro* 1,5-shifts calculated at the B3LYP/6-31G** level, the NICS(0) values calculated at the B3LYP/6-311+G**//B3LYP/6-31G** level, tables containing the most important bond lengths, and Cartesian coordinates of all optimized geometries with total energies (au) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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