Chemical Reactivity in the $\{N, N_S, v(\mathbf{r})\}$ Space

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A reactivity picture developed within the spin-polarized density functional theory defined in the $E\{N, N_S, v(\mathbf{r})\}$ space is discussed. The reactivity model including changes in the total number of electrons N, the spin number (unpaired electron number) N_S, and the external potential $v(\mathbf{r})$ is tested against two chemical processes involving radical species. They are the hydrogenation reaction of the succinimidyl radical and the Bergman cyclization. Although the former reaction appears to be mostly driven by the spin potential, a quantity measuring the variations in electronic energy with respect to the spin multiplicity changes; the latter presents highly electrocyclic character without significant spin-polarization effects.

1. Introduction

The description of a chemical processes in terms of reactivity indices has became a current approach in theoretical chemistry. The progress made in this area has been strongly stimulated by the advances made in conceptual density functional theory (DFT), where the reactivity indices have been cast into the form of global and local static response functions. Although the former correspond to the first and higher derivatives of the electronic energy E with respect to the number of electrons N at fixed external potential of $v(\mathbf{r})$,[1−3] the latter are related to the derivatives of the electron density $\rho(\mathbf{r})$ or the electronic chemical potential μ with respect to the external potential.[4,5] For instance, the first derivative of the electronic energy with respect to N defines the electronic chemical potential[2] (the negative of electronegativity). This reactivity index describes the amount and direction of charge transfer involved in a chemical reaction. The second derivative of E with respect to N, however, quantitatively defines the hardness η introduced by Pearson.[3] The inverse of the chemical hardness $S = {}^1/_\eta$ is the global softness.[6] Although the concept of chemical hardness has been widely used to predict the stability of molecular systems through the maximum hardness principle,[7,8] the concepts of chemical softness and hardness form the principal ingredients of another empirical reactivity rule, namely, the HSAB principle.[9,10] Besides these global indices, there are a number of local descriptors of regional reactivity that have been connected with the selectivity of molecules toward specific reactions.[11,12] The most important of them is the Fukui function $f(\mathbf{r})$, which condenses in a single number the essentials of the frontier molecular orbital theory.[4] It has been given an operational definition as the derivative of the electron density with respect to the change in the total number of electrons in the system. The sites where this reactivity index displays a high value are associated with the active regions in the molecule. Whereas, the local softness, defined as $s(\mathbf{r}) = f(\mathbf{r})\, S$, describes the most polarizable sites in a molecule (i.e., those sites where the exchange of electronic charge with the environment is highly favored). Note that the Fukui function has the additional property of projecting in the different molecular regions a global property (for instance, the global softness). The set of global and local electronic indices defined in the $\{\rho(\mathbf{r}), v(\mathbf{r})\}$ representation of DFT may conveniently describe those chemical processes where the spin multiplicity of the reacting system is strictly conserved according to the general selection rule stating that in a chemical reaction the total spin angular momentum is not subjected to change. There may be, however, some chemical processes where despite the total spin conservation rule the reagents may change their spin multiplicity. As clearly stated by Buchachenko,[13] the spin chemistry introduces magnetic interactions that contribute almost nothing to the chemical energy, being negligibly small and traditionally ignored; however, only some of these magnetic interactions are able to change the electron spin of reactants and switch the reaction between spin-allowed and spin-forbidden channels**.** Consider, for instance, the spin catalytic effects of paramagnetic species.[14−16]

Within a theoretical framework, the total spin conservation may be guaranteed only if the whole reacting system (including spin catalysts) is considered within a supermolecule scheme. The spin space is increased now. Standard spin angular momentum sum rules produce new spin states (that conserves the total spin angular momentum) that could be available for the system to evolve into the state of products following the spin conservation. Despite the fact that the static reactivity model that consider one reactant as a substrate and the other as the external perturbing reagent may apparently violate the spin conservation rule, it may provide useful information about the propensity of the system to modify its spin multiplicity toward the allowed spin states that guarantee the total spin conservation. The incorporation of spin polarization effects associated with the changes in spin multiplicity may be conveniently described in an enlarged representation $\{\rho(\mathbf{r}), \rho_S(\mathbf{r}), v(\mathbf{r})\}$ that incorporates the spin density $\rho_S(\mathbf{r})$ defined as the difference between the spin-up (α) and spin-down (β) populations. The general formalism has been fully described previously.[17−19] In the present work,

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we intend to illustrate the practical implementation of the spin-polarized density functional theory and its potential usefulness in describing the chemical reactivity of radical species.

2. General Formalism

The generalized (spin-polarized) representation $E\{\rho(\mathbf{r}), \rho_S(\mathbf{r}), v(\mathbf{r})\}$ proposed by Galván, Vela, and Gázquez[17] can be conveniently used to describe chemical processes where not only charge-transfer processes are present in a chemical reaction but also spin-polarization effects may be incorporated. It contains as the basic variables the electron density, defined as $\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})$, the spin density, defined as $\rho_S(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$, and the external potential $v(\mathbf{r})$ due to the compensating positive (nuclear) charges in the system. Both densities are constrained to follow the normalization conditions

$$N = \int d\vec{r}\ \rho(\vec{r}) = \int d\vec{r}\ \rho_\alpha(\vec{r}) + \int d\vec{r}\ \rho_\beta(\vec{r}) = N_\alpha + N_\beta \tag{1}$$

$$N_S = \int d\vec{r}\ \rho_S(\vec{r}) = \int d\vec{r}\ \rho_\alpha(\vec{r}) - \int d\vec{r}\ \rho_\beta(\vec{r}) = N_\alpha - N_\beta \tag{2}$$

Using these normalization conditions, it is possible to define an equivalent representation $E\{N, N_S, v(\mathbf{r})\}$.[17,19] In this representation, a Taylor series expansion of the total energy, retaining terms up to second order, acquires the form

$$\begin{aligned}\Delta E \cong \mu_N \Delta N + \mu_S \Delta N_S + \int d\mathbf{r}\ \rho(\mathbf{r})\ \Delta v(\mathbf{r}) + \frac{1}{2}\eta_{NN}(\Delta N)^2 + \\ \eta_{NS}\Delta N \Delta N_S + \frac{1}{2}\eta_{SS}(\Delta N_S)^2 + \Delta N \int d\mathbf{r}\ f_{NN}\ \Delta v(\mathbf{r}) + \\ \Delta N_S \int d\mathbf{r}\ f_{NS}\ \Delta v(\mathbf{r}) + \frac{1}{2}\int\int d\mathbf{r}\ d\mathbf{r}'\ \chi(\mathbf{r}, \mathbf{r}')\ \Delta v(\mathbf{r})\ \Delta v(\mathbf{r}') + \\ \ldots\end{aligned} \tag{3}$$

where

$$\mu_N = \left[\frac{\partial E}{\partial N}\right]_{N_S, v(\vec{r})} \tag{4}$$

is a quantity related to the electronic chemical potential μ defined in the $\{N, v(\mathbf{r})\}$ representation.[1] The spin potential μ_S has been defined as[17-19]

$$\mu_S = \left[\frac{\partial E}{\partial N_S}\right]_{N, v(\vec{r})} \tag{5}$$

which accounts for the changes in electronic energy induced by variations in the spin multiplicity at fixed N and $v(\mathbf{r})$.

The quantities η_{NN},η_{SN}, η_{NS}, and η_{SS} are the generalized hardness parameters introduced by Galvan et al.[17]

$$\eta_{NN} = \left(\frac{\partial \mu_N}{\partial N}\right)_{N_S, v(r)} \tag{6}$$

$$\eta_{NS} = \left(\frac{\partial \mu_N}{\partial N_S}\right)_{N, v(r)} = \left(\frac{\partial \mu_S}{\partial N}\right)_{N_S, v(r)} = \eta_{SN} \tag{7}$$

$$\eta_{SS} = \left(\frac{\partial \mu_S}{\partial N_S}\right)_{N, v(r)} \tag{8}$$

The Fukui functions in eq 3 were defined in that generalized formalism as[17,19]

$$f_{NN} = \left(\frac{\partial \rho}{\partial N}\right)_{N_S, v(\vec{r})} \tag{9}$$

$$f_{NS} = \left(\frac{\partial \rho}{\partial N_S}\right)_{N, v(\vec{r})} \tag{10}$$

and the term $\chi(\mathbf{r}, \mathbf{r}')$is the linear response function.[1]

The first-order change in electronic energy is given by

$$\Delta E = \mu_N \Delta N + \mu_S \Delta N_S + \int d\mathbf{r}\ \rho(\mathbf{r})\ \Delta v(\mathbf{r}) \tag{11}$$

We may think of both of the μ_N and μ_S indices as also being functions of N and N_S and a functional of $v(\mathbf{r})$ so that the exact differential for the electronic and spin potentials may be written as

$$\Delta \mu_N = \eta_{NN}\Delta N + \eta_{NS}\Delta N_S + \int d\vec{r}\ f_{NN}(\vec{r})\ \Delta v(\vec{r}) \tag{12}$$

$$\Delta \mu_S = \eta_{SN}\Delta N + \eta_{SS}\Delta N_S + \int d\vec{r}\ f_{NS}(\vec{r})\ \Delta v(\vec{r}) \tag{13}$$

Equations 3−13 are the basic expressions used to describe the chemical reactivity in the spin-polarized framework. Whereas eq 3 describes the total energy changes in the system, eqs 4−10 provide a complete set of reactivity indices that allow us to understand those chemical processes where N, N_S, and $v(\mathbf{r})$ vary. The formalism outlined above is based on trajectories at fixed N or N_S. Therefore, the derivative defined in eq 4 does not correspond to the standard chemical potential.[18] Nevertheless, eq 3 describes a state functional in $\{N, N_S\}$ space[19]; therefore, formally we can define the change between any two states as a combination of two steps—one at fixed N and other at fixed N_S. In practice, it is possible to use Janak's extension of the Khon−Sham theory[1] to study these kinds of processes with fractional occupation numbers.[18] The physical meaning of the trajectories in the $\{N, N_S\}$ space is certainly restricted to vertical transitions between states of different multiplicities; this situation has been exploited to study singlet−triplet gaps.[20] In the case of trajectories at fixed N_S, the reactivity indices defined in eqs 4, 6, and 9 are suitable, for example, to address processes where coordination bonds are formed.

The local indices $f_{NN}(\mathbf{r})$ and $f_{NS}(\mathbf{r})$ may be approached by a finite difference procedure described in earliest work[21−23] in terms of the MO coefficients and the overlap matrix. This model will be used to examine two well-documented reactions involving radical species, namely, the hydrogenation reaction of the succinimidyl radical and the cyclization of an enediyne to *p*-benzyne. The first one represents a case where there is a change in N_S, and the second one occurs at constant N_S.

3. Computational Details

The geometry optimization of the ground- and transition-state structures involved in both reactions were performed using the Gaussian 98 suite of programs[24] at the UDFT level of theory. The hybrid B3LYP functional was chosen together with the 6-31G(d) basis set for the Bergman reaction. For the hydrogenation reaction of succinimidyl, the location of the TS structure required a higher B3LYP/6-311G(d) level of theory because the appropriated description of hydrogen-transfer processes requires a basis set with enough flexibility around this atom. The electronic potential μ_N, the spin potential μ_S, and the $f_{NN}(\mathbf{r})$ and $f_{NS}(\mathbf{r})$ Fukui functions were calculated in terms of the

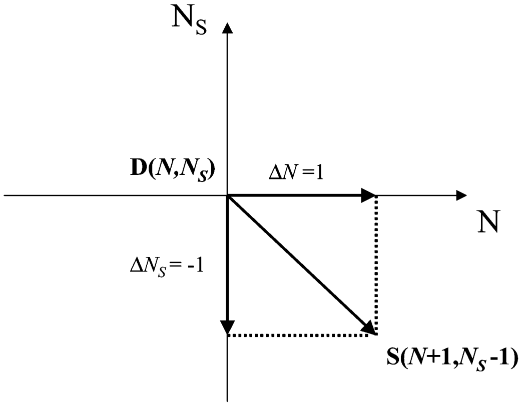

Figure 1. Schematic representation for the addition of a hydrogen atom to the doublet D ground state of the succiminidyl radical in the $\{N, N_S\}$ plane (at constant external potential) to end up in a singlet, S, state.

frontier molecular orbital HOMO and LUMO following the definitions given by Galván et.al.[17] The η_{NN} hardness has been defined as the smallest gap between the one-electron energies of the frontier molecular orbitals. Although the spin hardness η_{SS} has an approximate expression in terms of the spin potentials in the direction of increasing and decreasing multiplicity,[17,19] the η_{SN} parameter can be conveniently fixed for a particular case from the second-order energy variation in terms of μ_N^+, μ_S^- η_{NN}, η_{SS}, and ΔE. For instance, consider the particular cases of $\Delta N = 1$ and $\Delta N_S = -1$ (which is actually the case of the hydrogenation reaction of the succinimidyl radical). Using eq 3 and ignoring $\Delta v(\mathbf{r})$ changes, we get

$$\Delta E = \mu_N^+ - \mu_S^- + \frac{1}{2}\eta_{NN} + \frac{1}{2}\eta_{SS} - \eta_{NS} \qquad (14)$$

Solving for η_{NS} gives

$$\eta_{NS} = \mu_N^+ - \mu_S^- + \frac{1}{2}(\eta_{NN} + \eta_{SS}) - \Delta E \qquad (15)$$

4. Results and Discussion

4.1. Hydrogenation of the Succinimidyl Radical. The hydrogenation of the succinimidyl radical may be described by the following equation:

$$R\bullet + H\bullet \rightleftarrows RH \qquad (16)$$

To analyze the intrinsic reactivity of succinimidyl species toward hydrogenation, we shall consider it to be the substrate $R\bullet$ whereas the hydrogen atom will be considered to be an external perturbation. In other words, we intend to assess, within a static reactivity picture, the global and local response functions at the substrate, induced by the addition of one electron to it, which changes the spin number N_S. Within a first approximation, the changes in the external potential due to the presence of the perturbing reagent (the hydrogen atom) may be neglected because the attachment of a hydrogen atom to any larger group can be considered to be a limiting case for an external potential change in chemical reactions so that the process (eq 16) can be approximately represented in the $\{N, N_S\}$ plane, as described in Figure 1. Figure 2 shows the thermodynamic cycle used to mimic the hydrogenation process through the direct pathway for the conversion of the doublet $D(N, N_S)$ state associated with $R\bullet$ into the singlet $S(N+1, N_S-1)$ state of RH, which involves an energy change ΔE. An alternative way to achieve this process would be by a hypothetical change that implies the addition of one electron to the system, at constant multiplicity, entailing an energy cost ΔE_1, followed by an isoelectronic multiplicity change that involves an energy variation ΔE_2. As expected, $\Delta E = \Delta E_1 + \Delta E_2$. This alternative pathway implies the participation of a configurational intermediate state $D(N+1, N_S)$, which is reminiscent of the electronic transition state introduced by Slater to describe excitation energies in atoms.[25] The model used to describe the addition of an extra electron to the system at fixed spin multiplicity and the corresponding spin rearrangement to lead the RH singlet product are schematically displayed in Figure 3. Starting from the electronic configuration (a) that represents the doublet state of $R\bullet$, we form the Slater configurational transition state (CTS) (b) by adding half an electron in the α space (↿) and half an electron in the β space (⇂). The change from state (b) to state (c) leads to a singlet product. The last step is simply a spin rearrangement that accounts for the spin-polarization contribution to process 16. In the present case, the direct pathway shown in Figure 2 is a suitable method by which to obtain the energy changes associated with reaction 16. Then, using $\Delta N = 1$ and $\Delta N_S = -1$ and setting $\delta v(\mathbf{r}) = 0$ in the corresponding equations (11−13), we obtain the particular expressions

$$\begin{tikzcd} D(N,N_S) \arrow[r, "\Delta E_1"] \arrow[dr, "\Delta E"'] & D(N+1,N_S) \arrow[d, "\Delta E_2"] \\ & S(N+1,N_S-1) \end{tikzcd}$$

Figure 2. Possible pathways for the addition of a hydrogen atom to the singlet ground state of the succiminidyl radical.

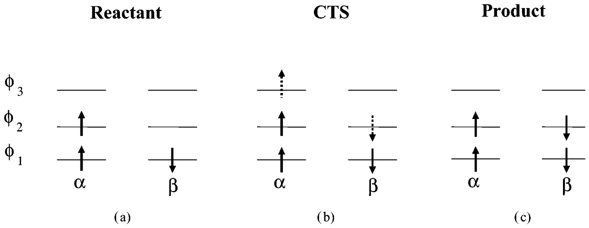

Figure 3. Hypothetical electronic process to mimic the addition of a hydrogen atom to the singlet ground state of the succiminidyl radical (a). State (b) is the configurational or electronic Slater transition state, where half an electron (↿) and (⇂) has been added to the α and β spaces, respectively, to increase the number of electrons in one unit at constant multiplicity. State (c) is the singlet ground state of the hydrogenated product.

$$\Delta E = \mu_N^+ - \mu_S^- \qquad (17a)$$

$$\Delta\mu_N^0 = \eta_{NN} - \eta_{NS} \qquad (17b)$$

$$\Delta\mu_S^0 = \eta_{SN} - \eta_{SS} \qquad (17c)$$

where μ_N^+ and μ_S^- are the electronic chemical potential in the direction of $N \rightarrow N+1$ and the spin potential in the direction of $N_S \rightarrow N_S - 1$, respectively.

The present model may be complemented with Parr's reactivity criterion based on the variation of the electronic chemical potential.[1] This author suggested that a large negative value of the change in the electronic chemical potential is good

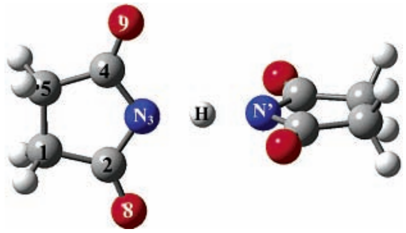

Figure 4. Optimized transition-state structure for the hydrogen transfer between the succinimidyl radical and succinimide and atom numbering.

TABLE 1: Electronic and Spin Quantities for the Hydrogenation Reaction of the Succinimidyl Radical[a]

μ_N^+	μ_S^-	η_{NN}	η_{SS}	η_{NS}	$\Delta\mu_N{}^\circ$	$\Delta\mu_S{}^\circ$
−0.1330	0.0438	0.0281	−0.0319	−0.1787	0.2068	−0.1468

$\Delta\mu_N{}^\circ$	$\Delta\mu_S{}^\circ$	$\Sigma f_{NN}\Delta v_A$	$\Sigma f_{NS}\Delta v_A$	$\Delta\mu_N$	$\Delta\mu_S$
0.2068	−0.1468	−0.0847	0.0111	0.1221	−0.1357

[a] Superscript (°) refers to calculations without corrections for external potential. All values are given in au.

for the reaction to proceed. A similar criterion can be formulated around the spin-potential change in a radical process. Moreover, the comparison between $\Delta\mu_N$ and $\Delta\mu_S$ introduces an additional reactivity criterion. For instance, if $\Delta\mu_N$ is large and negative with respect to $\Delta\mu_S$, then the process will be controlled by the charge transfer. Conversely, if $\Delta\mu_S$ is large and negative with respect to $\Delta\mu_N$, then the driving potential will be the spin-polarization contribution.

To test the model described above for reaction 16, we chose an isodesmic process involving the hydrogen atom transfer between the succinimidyl radical and succinimide. This choice makes the location of the transition-state structure involved in the hydrogen migration easier. The transition-state structure that was obtained was characterized by a unique imaginary frequency of 2026i cm^{-1} and corresponds to a perpendicular arrangement of the five-membered rings with the hydrogen located at the midpoint of the N−N′ distance, as shown in Figure 4. The global indices for the succinimidyl ground state, neglecting the changes in external potential, are summarized in Table 1, first entry. It may be seen that whereas the change in the electronic chemical potential ($\Delta\mu_N^0$) is positive for this reaction, the change in the spin potential ($\Delta\mu_S^0$) is negative, thereby indicating that charge transfer is an unfavorable event at the beginning of the reaction whereas the spin-polarization change seems to be a more favorable process. These results that were obtained within a simplified model, where the variation in the external potential due to the presence of the perturbing reagent was neglected, may be corrected by adding the contribution from the changes in the external potential given by the last terms in eqs 12 and 13. These integrals may be approached by[26]

$$\int \mathrm{d}\vec{r}\, f_{NN}(\vec{r})\, \delta v(\vec{r}) = \sum_A f_{NN}^A \Delta v_A \tag{18}$$

$$\int \mathrm{d}\vec{r}\, f_{NS}(\vec{r})\, \delta v(\vec{r}) = \sum_A f_{NS}^A \Delta v_A \tag{19}$$

where the quantity Δv_A accounts for the electrostatic effects in the radical species induced by changes in geometry along the reaction coordinate. It was approached by

$$\Delta v_A = \sum_{B\neq A} \frac{\Delta \mathbf{q}_B}{R_{AB}} - \sum_{B\neq A} \frac{\mathbf{q}_B}{R_{AB}^2} \Delta R_{AB} \tag{20}$$

TABLE 2: Charges Variations $\Delta\mathbf{q}_B$, External Potential Variations Δv_A, and the Corresponding Regional Fukui Functions at Each Site of the Succinimidyl Radical[a]

site$_A$	$\Delta\mathbf{q}_B$	Δv_A	f_{NN}^+	f_{NS}^-	$f_{NN}^+\Delta v_A$	$f_{NS}^-\Delta v_A$
C_1	−0.003	−0.070	0.028	−0.025	−0.002	0.002
N_3	−0.164	0.014	0.042	0.196	0.001	0.003
C_4	0.048	−0.168	0.178	0.003	−0.030	−0.001
H_6	−0.006	−0.057	0.009	−0.001	−0.001	0.000
O_8	−0.054	−0.039	0.255	−0.076	−0.010	0.003
H_{10}	−0.006	−0.057	0.009	−0.001	−0.001	0.000

[a] $\Delta\mathbf{q}_B$ values are given in units of electrons, and Δv_A values are given in atomic units. All values are given in au.

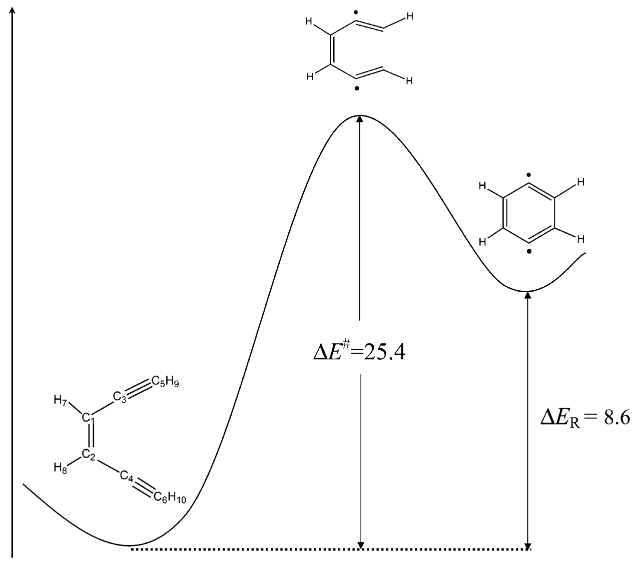

Figure 5. Potential energy profile for the Bergman cyclization.

with $\Delta\mathbf{q}_B$ representing the variations in Mulliken atomic charges for the set of atoms $B\neq A$, between the ground state of the substrate and their corresponding structure at the transition state whereas the interatomic distance R_{AB} refers only to the initial geometry of the succinimidyl radical. The second term in eq 20 corresponds to corrections of second order in the geometrical parameters; therefore, they have small contributions and can be neglected. The results of this additional calculation are displayed in Table 1, second entry. It may be seen that the incorporation of the corrections in the external potential does not qualitatively modify the previous result. Therefore, on the basis of Parr's criterion for $\Delta\mu_N$ and the additional criterion for $\Delta\mu_S$ with respect to $\Delta\mu_N$, we may conclude that the hydrogenation of the succinimidyl radical is due mostly to a spin-polarization change rather than to charge transfer. Table 2 shows the results for the local reactivity analysis. It is interesting that whereas the Fukui function $f_{NN}(\mathbf{r})$ in the direction of an increasing number of electrons is almost irrelevant at the nitrogen atom (the hydrogenating site) the Fukui function $f_{NS}(\mathbf{r})$, accounting for the variation in the electron density with respect to the changes in the spin number N_S in the direction of decreasing N_S, consistently shows its highest value at the nitrogen site.

4.2. Bergman Cyclization. The Bergman reaction has concentrated a large number of theoretical studies in the past few years.[27−29] Figure 5 depicts the cyclization of an enedyine to yield the aromatic biradical product *p*-benzyne. The optimized structures and energetic parameters are shown in Table 3 and Figure 5, respectively. The transition state has a unique imaginary frequency at 431i cm^{-1}. For this chemical reaction, the electron and the spin density are redistributed without net

TABLE 3: Geometrical Parameters for the Bergman Reaction[a]

	reactant	TS	product
d(C1−C2)	1.37	1.41	1.48
d(C1−C3)	1.42	1.4	1.35
d(C3−C5)	1.22	1.28	1.35
d(C5−C6)	4.53	2.06	1.48
A(C2−C1−C3)	125.7	119.0	117.8
A(C1−C3−C5)	177.2	134.9	124.3

[a] All of the structures are planar. Bond lengths are given in angstroms, and angles, in degrees.

TABLE 4: Charge Variations $\Delta \mathbf{q}_B$, External Potential Variations $\Delta \upsilon_A$, the Fukui Functions at Each Site of Enediyne, and the Corresponding External Potential Correction Per Site $f^0_{NN}\Delta\upsilon_A$[a]

site_A	$\Delta \mathbf{q}_B$	$\Delta \upsilon_A$	f^0_{NN}	f^0_{NS}	$f^0_{NN}\Delta\upsilon_A$
C_1	−0.036	−0.068	0.226	0.000	−0.015
C_3	−0.154	0.135	0.051	0.000	0.007
C_5	0.244	−0.192	0.223	0.000	−0.043
H_7	−0.005	−0.061	0.000	0.000	0.000
H_9	−0.048	0.147	0.000	0.000	0.000

[a] All values are given in u.a.

changes in N or N_S; the variations in μ_N and μ_S given by eqs 12 and 13 will be reduced to

$$d\mu_N = \int d\vec{r}\, f^0_{NN}(\vec{r})\, \delta\upsilon(\vec{r}) \qquad (21a)$$

and

$$d\mu_S = \int d\vec{r}\, f^0_{NS}(\vec{r})\, \delta\upsilon(\vec{r}) \qquad (21b)$$

Because we are dealing with a singlet state along the whole reaction path, the corresponding Fukui functions in this case have been taken as the average of the Fukui function in the directions of increasing (+) and decreasing (−) electron and spin numbers. Table 4 summarizes the information necessary to approach the electronic- and spin-potential variations described by eqs 21a and 21b, respectively. The result is $\Delta\mu_N = -0.1024$ ua, and $\Delta\mu_S$ is zero because the average $f_{NS}(\mathbf{r})$ is zero for all of the sites in the reactant. Note that here again there is consistency between the driving potential and the local reactivity picture given by the electronic Fukui function $f_{NN}(\mathbf{r})$. They display the highest values at the C1, C2, C5, and C6 centers. Note also the relatively high values of the $f^0_{NN}\,\Delta\nu_A$ contribution from the C5 and C6 centers, describing that the major changes for the intramolecular rearrangement come from the terminal carbon atoms of the enedyine. On the basis of these results and using the same criteria described above, we may conclude that the Bergman reaction is driven by the electronic chemical potential and therefore controlled by an intramolecular charge transfer. This means that the closure of the enedyine to *p*-benzyne is an electrocyclic rather than a radical process, similar to that involved in the closure of butadiene to cyclobutene. This result is in close agreement with the experimental observation that in this isomerization process the biradical character appears late in the reaction.[30] Other theoretical studies seem to confirm this result.[28]

5. Concluding Remarks

A generalized density functional reactivity model incorporating spin-polarization effects has been discussed for two well-documented reactions involving radical species. The first one occurs with a change in the spin number, N_S, of the substrate whereas the second one does not imply any change in N_S. The formalism introduces new global and local reactivity indices as well as a new criterion of reactivity, which is based on the changes in electronic and spin potentials within a static reactivity picture developed around the ground states of reactants. The reactivity picture introduces new insight into the theoretical study of those chemical processes presenting spin-polarization rearrangement along the reaction coordinate. The spin potential as well as the electronic chemical potential consistently complement the local reactivity picture, which in turn is described by their first derivatives with respect to the external potential, namely, the Fukui functions f_{NN} and f_{NS}, respectively.

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