

# Understanding the polar character trend in a series of Diels-Alder reactions using molecular quantum similarity and chemical reactivity descriptors.

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**A. On the Density Functional Theory (DFT) and the chemistry reactivity problem:  
role of the charge transfer in Diels-Alder reactions.**

Based on the Hohenberg and Kohn (HK) theorems [1], Density Functional Theory (DFT) represents an attractive reformulation of the electronic problem associated to ground states, where *the electron density  $\rho(\mathbf{r})$  - and not the wave-function  $\Psi(\mathbf{r};\mathbf{R})$  - acquires the preponderant role for the determination of all the quantum mechanics observables* [2]. In this sense, the  $(\rho(\mathbf{r}))$  uniquely determines the **external potential**  $v(\mathbf{r}) = \sum_{\alpha} Z_{\alpha}/|\mathbf{r} - \mathbf{R}_{\alpha}|$ , the **electron number** ( $N$ ) defines the **electronic Hamiltonian**, and therefore the **Schrödinger equation**, the **electronic energy**  $E[\rho]$  and others quantum observables. In our notation  $(\mathbf{r})$  represents the electronics coordinate, whereas  $(Z_{\alpha})$  and  $(\mathbf{R}_{\alpha})$  represent the atomic number and nucleus coordinate in the system. The energy functional can be written as:

$$E[\rho] = F[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} , \quad \text{A.}$$

Where  $F[\rho] = T[\rho] + V_{ee}[\rho]$  is a function that includes universal electronics terms as kinetic energy  $T[\rho]$  and the electron-electron interaction  $V_{ee}[\rho]$ . The second terms in (A1) represents the nuclear-electron potential interaction in the system. HK theorems also stipulate that  $\rho(\mathbf{r})$  is solution of a **variational principle**  $\delta\{E[\rho] - \mu N[\rho]\} = 0$  [2], and the Lagrange multiplier ( $\mu$ ) is associated to the **normalization condition** of the densities,  $N[\rho] = \int \rho(\mathbf{r})d\mathbf{r}$ . The three-dimensional electron density is the key variable in DFT context and the electronic ground state energy is subject to the variational principle with respect to the density,  $\mu = [\delta E / \delta \rho]_v = v(\mathbf{r}) + \delta F / \delta \rho(\mathbf{r})$ . The chemical potential in DFT is a measure of the tendency to escape of the electron from the electronic cloud, and is a similar amount to the chemical potential of the macroscopic thermodynamic. Parr et al. shown that this parameter corresponds to the negative of the Milliken electronegativity,  $\mu = -\chi_M$ , establishing a connection between the concept of electronegativity and chemical formalism in DFT [3,4]. This is the origin of DFT conceptual [4, 5]. In this context, **the electron density variations (e.g., treated in a perturbative scheme) are the bases to the rationalizing of the chemical reactivity of the systems** [6]. DFT is a fruitful framework for the definition and exploration of many chemical concepts that have a strong element of intuition and empiricism. Concepts such as electronegativity, hardness, softness, selectivity, activation energy, etc., are in fact the basis of the chemical interpretation associated with chemical reactivity theories [7]. This conceptual framework is a general reference for the development of the goals in this study.

In the DFT context the electronic ground state at zero temperature is analogous to the equilibrium state of a macroscopic system, the electronic changes are assumed and represented in terms of changes from the ground state to another (i.e., reversible processes) [4]. A representation of the electron energy and the perturbative change can be expressed through a Taylor expansion of functional written in terms of the variables that specify the representation (or assembly) elected [5]. In the **canonical** representation (i.e., electronic

Hamiltonian) such variables are the electrons number and the external potential mentioned,  $E = E[N, v(\mathbf{r})]$ . Legendre transform (for example) are representation analogues that allows the construction of electronic analogues to the **grand canonical ensembles**.  $\Omega = \Omega[\mu, v(\mathbf{r})] = E[N, v(\mathbf{r})] - \mu N$ , **isomorphic**  $F = F[N, \sigma(\mathbf{r})] = E[N, v(\mathbf{r})] - \int v(\mathbf{r})\sigma(\mathbf{r})d\mathbf{r}$ , and **grand isomorphic**  $R = R[\mu, \sigma(\mathbf{r})] = F[N, \sigma(\mathbf{r})] - \mu N$ , whose **responses functions** can be associates with important chemistry concepts. In this formalism  $\sigma(\mathbf{r})$  represents form factor therefore  $\rho(\mathbf{r}) = N\sigma(\mathbf{r})$ . In DFT the fundamental relations for the differential change of the ground state (first order) in simple terms can be written in terms of response rates essentially linear and symmetrical [4,5,7].

$$\begin{aligned}
 dE &= \left[ \frac{\partial E}{\partial N} \right]_{v(\mathbf{r})} dN + \int \left[ \frac{\delta E}{\delta v(\mathbf{r})} \right]_N \delta v(\mathbf{r}) d\mathbf{r}, \\
 d\Omega &= \left[ \frac{\partial \Omega}{\partial \mu} \right]_{v(\mathbf{r})} d\mu + \int \left[ \frac{\delta \Omega}{\delta v(\mathbf{r})} \right]_{\mu} \delta v(\mathbf{r}) d\mathbf{r}, \\
 dF &= \left[ \frac{\partial F}{\partial N} \right]_{\sigma(\mathbf{r})} dN + \int \left[ \frac{\delta F}{\delta \sigma(\mathbf{r})} \right]_N \delta \sigma(\mathbf{r}) d\mathbf{r}, \\
 dR &= \left[ \frac{\partial R}{\partial \mu} \right]_{\sigma(\mathbf{r})} d\mu + \int \left[ \frac{\delta R}{\delta v(\mathbf{r})} \right]_{\mu} \delta v(\mathbf{r}) d\mathbf{r}.
 \end{aligned}
 \tag{A}$$

Where the coefficients of the Taylor expansion, i.e.,  $[\delta \xi_1 / \delta \xi_2]_{\xi_3}$ , represent the “**answers**” **snapshots intrinsic of the energy of each representation** ( $\xi_1$ ) **to changes in the variables indicated in the denominator** ( $\xi_2$ ) **with the invariance under the restriction of the variable** ( $\xi_3$ ). Such amounts are considered here indexes or reactivity descriptors and form the basis for the development and exploration in this study.

The global nature indexes define global responses to global disturbances (that affect the system as a whole) and global responses to local disturbances or (equivalently) local responses to local disturbances. Such relation shows new reactivity indexes and has been directly related with chemical concepts fundamental, using results and representations associated to canonical and grand canonical ensembles where large changes in the electronic charge distribution can be considered as “answers” in the system [4, 7]. These changes, expressed as reorganizations of electron densities can be the starting point for the exploration of the Diels-Alder reactions studied.

Using a canonical representation for example to illustrate the above points, we found which the first-order rates is the **chemical potential**  $\mu \equiv [\partial E / \partial N]_{v(\mathbf{r})}$  (electronegativity negative) and the electron density (local probability in the density distribution)  $\rho(\mathbf{r}) \equiv [\delta E / \delta v(\mathbf{r})]_N = [\delta E / \delta v(\mathbf{r})]_N$ . The second order descriptors have been identified and

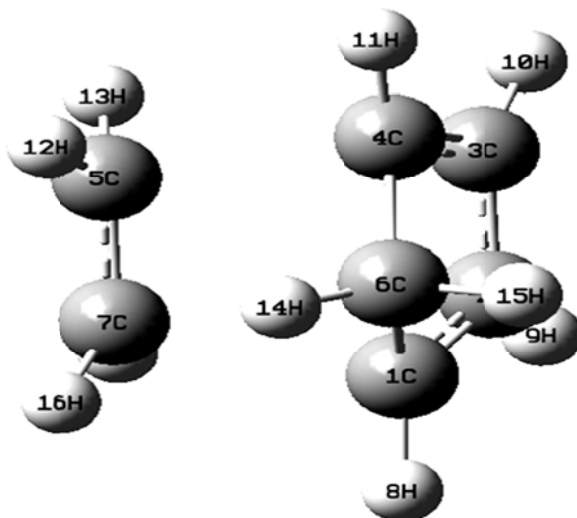
associated with the concepts of **chemical hardness**  $\eta \equiv [\partial\mu/\partial N]_{v(\mathbf{r})}$ , **Fukui function**  $f(\mathbf{r}) \equiv [\partial\rho(\mathbf{r})/\partial N]_{v(\mathbf{r})} = [\delta\mu/\delta v(\mathbf{r})]_N$  and the **linear response function of the density**  $\chi(\mathbf{r}, \mathbf{r}_1) \equiv [\delta\rho(\mathbf{r})/\delta v(\mathbf{r}_1)]_N$ . The **chemical softness** (formally defined in grand canonical ensemble  $s \equiv [\partial N/\partial\mu]_{v(\mathbf{r})}$ ) is a concept that represents the inverse of the global chemical hardness. **Such global descriptors and quantities are used in the relation of the empirical principles commonly used in routine work and in the chemical laboratory such as the Maximum Hardness Principle (MHP) and the principle of Hard and Soft Acids and Bases (HSAB) of Pearson.**

Such schemes are useful in empirical analysis of *charge transfer* in connection with the Sanderson equalization principle for the electronegativity, for example. The global descriptors are closely related to energy changes (and hence with thermodynamics concept) in the reactive processes. In this sense, the atomic and molecular electronic energy in the ground state is a continuous function of the electrons number. In DFT different descriptors (can be evaluated with integer N values) and are associated with the opposite response rate of the system on the *charge transfer* (e.g., donation or acceptance of electrons).

In this study, the discontinuity in the energy and their dependence in the electron number are exploited in DFT reactivity context (e.g.; different chemical responses in the electrophile and nucleophile interactions). In the context of the characterization of the charge transfer, the utility of the global electrophilicity (intrinsic descriptor,  $\omega = \mu^2/2\eta$ ), can be critical in the context of the specific aims in this study [6,7]. In this sense, *we explain and emphasize that the Fukui function is a generalization of the perturbative models introduced by the Fukui reactivity in terms of molecular orbitals that are the basis for the rationalization of the Woodward-Hoffmann rules [7].*

## B. Structure Coordinate (.xyz)

### I. TS-Et (reference state)

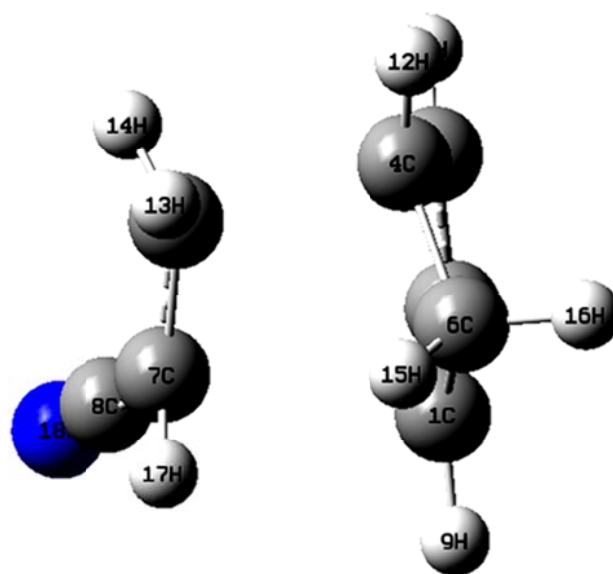


E(B+HF-LYP) = -272.6051 hartree, Imaginary Frequency:-515.90

symmetry c1

C	0.450031000	-1.163150000	0.362306000
C	1.194024000	-0.703449000	-0.744069000
C	1.192843000	0.706056000	-0.742949000
C	0.447932000	1.162661000	0.364102000
C	-1.613749000	0.699502000	-0.342205000
C	0.364350000	-0.001092000	1.339501000
C	-1.613669000	-0.700310000	-0.343112000
H	0.388219000	-2.201146000	0.670720000
H	1.585144000	-1.328822000	-1.538120000
H	1.582771000	1.333367000	-1.536055000
H	0.384082000	2.200044000	0.674141000
H	-2.074900000	1.246270000	0.476244000
H	-1.547847000	1.248842000	-1.275128000
H	-0.501261000	-0.002387000	2.003651000
H	1.275158000	-0.000772000	1.965065000
H	-2.074670000	-1.248208000	0.474676000
H	-1.547262000	-1.248493000	-1.276637000

## II. TS-1CN

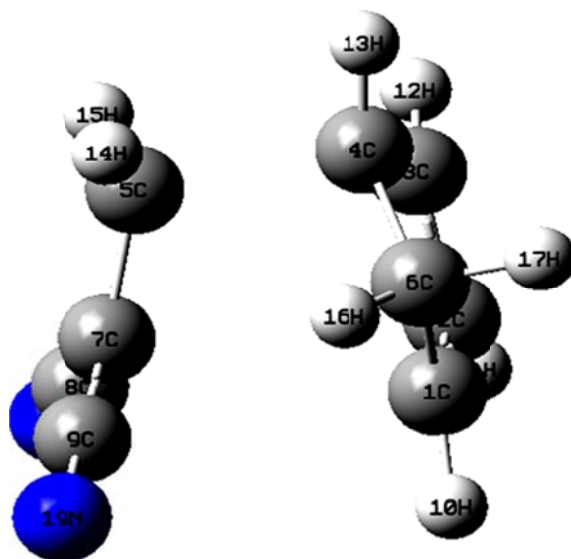


$E(\text{B+HF-LYP}) = -364.8267$  hartree, Imaginary Frequency:-462.95

symmetry c1

C	0.664109000	-0.868825000	1.044403000
C	0.579266000	-1.515268000	-0.193717000
C	1.163955000	-0.696367000	-1.181481000
C	1.557901000	0.532818000	-0.588931000
C	-0.190405000	1.563694000	-0.459388000
C	1.661744000	0.258505000	0.911635000
C	-0.995484000	0.897081000	0.491859000
C	-2.082167000	0.069294000	0.103366000
H	0.317607000	-1.268629000	1.989474000
H	0.052208000	-2.441753000	-0.381533000
H	1.173192000	-0.907802000	-2.243950000
H	2.213524000	1.240197000	-1.088037000
H	0.278678000	2.495529000	-0.153324000
H	-0.496722000	1.545630000	-1.500538000
H	1.495340000	1.117506000	1.563614000
H	2.673418000	-0.131195000	1.121514000
H	-0.987210000	1.211669000	1.530529000
N	-2.981935000	-0.615250000	-0.229175000

### III. TS-2CN

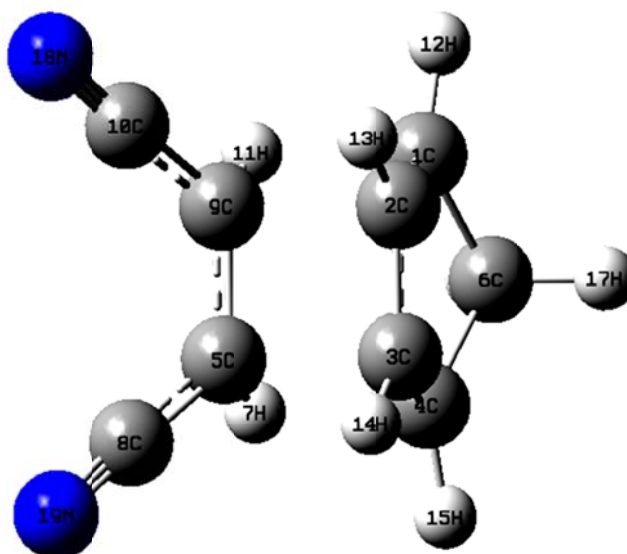


E(B+HF-LYP) = -457.0406 hartree, Imaginary Frequency:-365.22

symmetry c1

C	0.983168000	-0.429816000	-1.365256000
C	1.619592000	0.754174000	-1.016935000
C	2.073396000	0.657042000	0.320846000
C	1.606921000	-0.562200000	0.890000000
C	-0.178337000	-0.127991000	1.549805000
C	1.230364000	-1.456331000	-0.295929000
C	-1.068018000	0.136913000	0.465315000
C	-1.280202000	1.477149000	0.037918000
C	-1.882658000	-0.895495000	-0.077277000
H	0.490506000	-0.638935000	-2.306624000
H	1.691839000	1.637750000	-1.637002000
H	2.578707000	1.445154000	0.866408000
H	2.062495000	-0.979483000	1.784095000
H	-0.341976000	-1.061281000	2.083906000
H	0.054991000	0.708194000	2.201607000
H	0.411792000	-2.158777000	-0.132759000
H	2.119246000	-2.052996000	-0.567294000
N	-1.415080000	2.605501000	-0.270947000
N	-2.541057000	-1.779828000	-0.492377000

#### IV. TS-2cCN



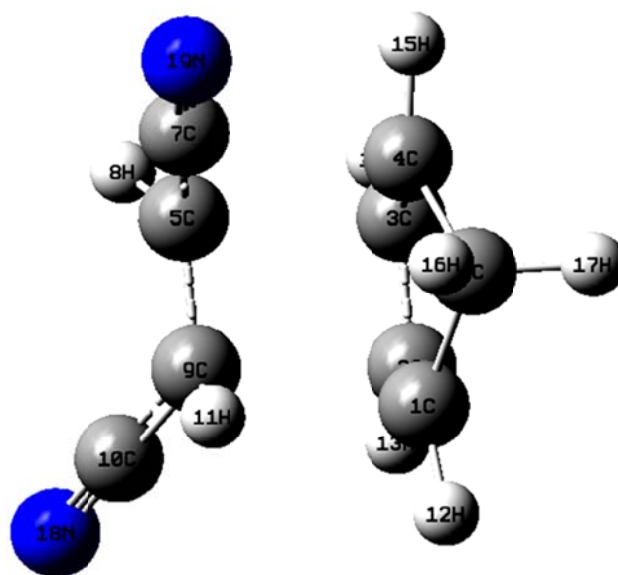
E(B+HF-LYP) = -457.0362 hartree, Imaginary Frequency:-480.43

symmetry c1

C	1.431963000	1.160655000	-0.044089000
C	1.173076000	0.702059000	1.268482000
C	1.172802000	-0.702139000	1.268376000
C	1.431340000	-1.160639000	-0.044347000
C	-0.517892000	-0.712806000	-0.985159000
C	2.056477000	-0.000035000	-0.799356000
H	-0.223629000	-1.204388000	-1.908140000
C	-1.417498000	-1.474872000	-0.176228000
C	-0.518086000	0.712854000	-0.985250000
C	-1.417596000	1.474930000	-0.176310000
H	-0.223633000	1.204536000	-1.908126000
H	1.590506000	2.200291000	-0.307115000
H	0.886261000	1.329045000	2.102701000
H	0.885773000	-1.329146000	2.102506000
H	1.589799000	-2.200296000	-0.307431000
H	1.910825000	0.000086000	-1.880787000
H	3.143193000	-0.000621000	-0.608930000
N	-2.137670000	2.128749000	0.482716000
N	-2.137560000	-2.128686000	0.482799000



## V. TS-2tCN

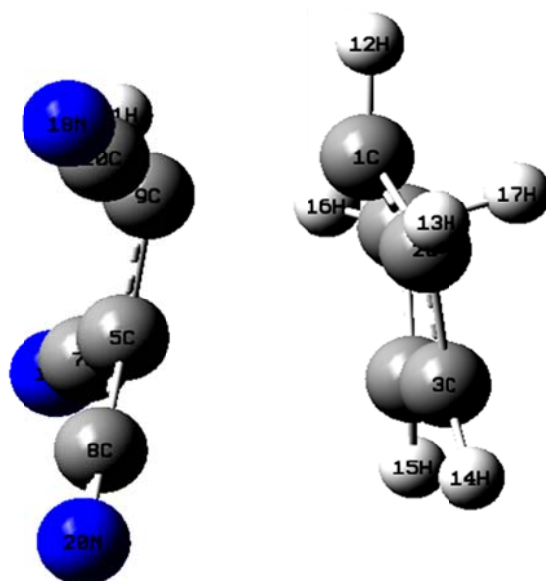


$E(\text{B+HF-LYP}) = -457.0388$  hartree, Imaginary Frequency:-468.11

symmetry c1

C	0.886833000	0.986009000	1.050949000
C	1.530345000	1.386540000	-0.145900000
C	0.553850000	1.659729000	-1.116831000
C	-0.725159000	1.446670000	-0.554418000
C	-0.723391000	-0.789920000	-0.516393000
C	-0.551257000	1.459379000	0.953756000
C	-2.104320000	-0.962964000	-0.194876000
H	-0.473132000	-0.937054000	-1.561682000
C	0.278136000	-1.047311000	0.465693000
C	1.531787000	-1.611353000	0.071086000
H	-0.045399000	-1.315159000	1.468043000
H	1.400426000	0.822220000	1.991530000
H	2.597930000	1.352986000	-0.320674000
H	0.750109000	1.881631000	-2.158525000
H	-1.663524000	1.674012000	-1.046556000
H	-1.287669000	0.890019000	1.521624000
H	-0.599681000	2.505570000	1.301101000
N	2.567733000	-2.065696000	-0.247565000
N	-3.244877000	-1.082146000	0.065671000

## VI. TS-3CN

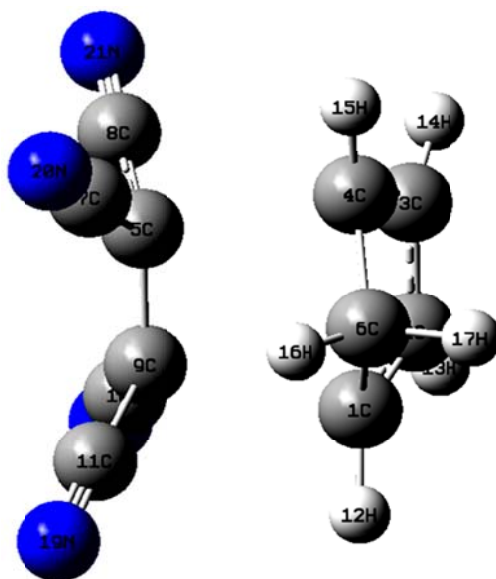


E(B+HF-LYP) = -549.2428 hartree, Imaginary Frequency:-381.60

symmetry c1

C	-0.81160000	1.467067000	-0.785579000
C	-1.359668000	1.549298000	0.533870000
C	-0.308270000	1.566658000	1.468897000
C	0.908761000	1.604030000	0.782220000
C	0.611794000	-0.842758000	-0.115164000
C	0.639828000	1.934604000	-0.660323000
C	1.951796000	-0.895109000	-0.594619000
C	0.316466000	-1.460182000	1.133442000
C	-0.444136000	-0.453267000	-1.021503000
C	-1.746083000	-1.063284000	-0.892304000
H	-0.126827000	-0.379257000	-2.061578000
H	-1.409277000	1.693057000	-1.664028000
H	-2.411781000	1.461747000	0.773935000
H	-0.422933000	1.473410000	2.540483000
H	1.894393000	1.587640000	1.230684000
H	1.348814000	1.517365000	-1.376235000
H	0.656640000	3.030759000	-0.787452000
N	-2.820322000	-1.527183000	-0.819267000
N	3.048154000	-0.917002000	-1.022435000
N	0.046117000	-1.959682000	2.163211000

## VII. TS-4CN



E(B+HF-LYP) = -641.4355 hartree, Imaginary Frequency:-433.61

symmetry c1

C	0.546796000	-1.156313000	1.466489000
C	1.877313000	-0.697676000	1.241072000
C	1.876973000	0.697603000	1.241412000
C	0.546177000	1.155501000	1.466970000
C	-0.324826000	0.734603000	-0.492696000
C	-0.216610000	-0.000757000	2.083299000
C	-1.575068000	1.418666000	-0.286717000
C	0.603040000	1.419124000	-1.355202000
C	-0.324558000	-0.734376000	-0.493354000
C	0.603740000	-1.417857000	-1.356156000
C	-1.574393000	-1.419192000	-0.287699000
H	0.277079000	-2.196329000	1.609804000
H	2.718450000	-1.328259000	0.985104000
H	2.717799000	1.328732000	0.985766000
H	0.276074000	2.195313000	1.611072000
H	-1.296144000	-0.001020000	1.933144000
H	-0.037922000	-0.000936000	3.171292000
N	1.373006000	-1.986452000	-2.034576000
N	-2.578178000	-1.991638000	-0.085295000
N	-2.579156000	1.990466000	-0.084029000
N	1.371922000	1.988558000	-2.033342000

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