

## Origin of the Synchronicity on the Transition Structures of Polar Diels–Alder Reactions. Are These Reactions [4 + 2] Processes?

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Received November 26, 2002

The transition structures (TSs) for a series of related Diels–Alder reactions between cyclopentadiene and mono-, di-, tri-, and tetracyanoethylene derivatives have been studied with use of DFT methods at the B3LYP/6-31G\* computational level. The increase of the electron-withdrawing substitution on ethylene increases the rate of these polar cycloadditions. However, the symmetric arrangement of cis and trans 1,2-di- and tetracyanoethylenes decreases the effectiveness of the substitution, which can be related to the symmetry found at the corresponding TSs. A DFT analysis of the global and local electrophilicity power of these series of cyano ethylenes provides a sound explanation about the nature of these synchronous processes. The present theoretical study is in agreement with the experimental outcomes.

### 1. Introduction

The Diels–Alder (DA) reaction is one of the most useful synthetic reactions in organic chemistry, and corresponds to one of a general class of cycloaddition reactions.<sup>1</sup> In it a 1,3-diene reacts with an olefinic or acetylenic dienophile to form an adduct with a six-membered ring. In the reaction two new  $\sigma$ -bonds are formed at the expense of two  $\pi$ -bonds in the starting material. The usefulness of the DA reaction arises from its versatility and from its remarkable stereochemistry. By varying the nature of the diene and dienophile many different types of carbocyclic structures can be built up. However, not all possibilities take place easily. For instance, the DA reaction between butadiene and ethylene must be forced to take place: after 17 h at 165 °C and 900 atm, it does give a yield of 78%.<sup>2</sup> The presence of electron-releasing substituents in the diene and electron-withdrawing (EW) in the dienophile or vice versa can drastically accelerate the process. Usually, 1,3-butadienes and cyclopentadienes react easily with electron-poor ethylenes.

In 1964, Sauer et al.<sup>3</sup> reported the reactivity of cyclopentadiene (**Cp**) with the cyanoethylene series in the DA reaction (see Table 1). An analysis of the relative rates shows that the rate increases with the cyano substitution

**TABLE 1. Rate Constants and Activation Energies (in kcal/mol) for the Diels–Alder Reaction of Dienophiles with Cyclopentadiene<sup>a,b</sup>**

	dienophile	$10^5 k$ [M <sup>-1</sup> s <sup>-1</sup> ]	$E_a$
<b>4CN</b>	tetracyanoethylene	$4.3 \times 10^7$	
<b>3CN</b>	tricyanoethylene	$4.8 \times 10^5$	
<b>2CN</b>	1,1-dicyanoethylene	$4.5 \times 10^4$	ca. 8.0 <sup>c</sup>
<b>2cCN</b>	maleonitrile	91	11.4 <sup>d</sup>
<b>2tCN</b>	fumaronitrile	81	12.6 <sup>d</sup>
<b>1CN</b>	acrylonitrile	1.04	15.2 <sup>e</sup>

<sup>a</sup> At 20 °C in dioxane. See ref 3. <sup>b</sup> The rate constant for **Cp** + **Et** cycloaddition has been estimated in 10<sup>-5</sup> (gas-phase data). See ref 4. <sup>c</sup> Reference 8. <sup>d</sup> Reference 3. <sup>e</sup> Reference 3.

on ethylene. However, it is easy to see that the successive substitution on the C1 and C2 carbon atoms has a different incidence. For instance, while 1,1-dicyanoethylene (**2CN**) is more than 10 000 times faster than cyanoethylene (**1CN**), *cis*- and *trans*-1,2-dicyanoethylene (**2cCN** and **2tCN**) are only ca. 100 times faster. In addition, tetracyanoethylene (**4CN**), the most reactive dienophile within the series, is only 100 times faster than tricyanoethylene (**3CN**) (see Table 1). These results indicate that the symmetric substitution at the C1 and C2 carbon atom of ethylene has a loss of effectiveness of the EW effect of the substitution.

The mechanism of the DA reaction has been controversial for some time.<sup>5</sup> The archetypal DA reaction of butadiene and ethylene is exothermic by 40 kcal/mol and has a reaction barrier of 27.5 kcal/mol.<sup>2</sup> It may occur via

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either a synchronous concerted mechanism associated with a pericyclic process or a stepwise mechanism involving the formation of diradical intermediates,<sup>5,6</sup> both mechanisms being very unfavorable. The butadiene + ethylene reaction, however, is not the typical case. In general, the DA reaction requires opposite electronic features of the substituents at the diene and the dienophile ends for the reaction to be reasonably fast. Furthermore, this type of substitution favors an asynchronous concerted mechanism.<sup>7–9</sup> In addition, adequate substitution on the diene and dienophile, which can favor the stabilization of charges of opposite signs, can give a stepwise mechanism with a large polar character.<sup>9</sup> Therefore, the molecular mechanism of these polar DA reactions can be located in the borderline between a highly asynchronous but concerted mechanism and a stepwise process with a large ionic character.

For a long time Domingo's group has been interested in the study of the molecular mechanism of the polar DA reactions.<sup>10–12</sup> For these reactions two mechanisms have been characterized: one corresponding to a one-step process through a highly asynchronous transition structure (TS),<sup>10</sup> and other corresponding to a two-step mechanism via a zwitterionic intermediate.<sup>11</sup> These studies point out a relationship between the decrease of the activation barrier of the cycloaddition and the charge transfer along a nonsynchronous bond-formation process. Thus, the increase of the electron-rich character of the diene (the nucleophilicity) together with the increase of the electron-poor character of the ethylene derivative (the electrophilicity), or vice versa, results in an increase in the charge transfer with a decrease of the activation barrier.<sup>10c</sup>

Recently, we reported the use of the global electrophilicity index,  $\omega$ , proposed by Parr et al.<sup>13</sup> to classify the global electrophilicity of a series of dienes and dienophiles currently present in DA reactions.<sup>14</sup> We found a good correlation between the difference in electrophilicity for the diene and dienophile pair,  $\Delta\omega$ , and the feasibility of the cycloaddition. In addition, the static charge-transfer

model proposed by Pearson<sup>15</sup> gave a good correlation with the actual charge transfer found at the corresponding highly asynchronous TSs.<sup>14</sup> Therefore,  $\Delta\omega$  for a diene/dienophile pair is a valuable tool to predict the polar character of a DA reaction. In addition, the proposed local electrophilicity index,  $\omega_k$ ,<sup>16</sup> also has been found to be a useful tool that correctly explains the regioselectivity of the polar Diels–Alder reactions. This model together with the Fukui functions for nucleophilic attack,  $f_k^+$ , and for electrophilic attack,  $f_k^-$ , allows the identification of the most electrophilic and nucleophilic centers in the reactants. Concurrent studies in polar DA reactions have evidenced the feasibility of  $\Delta\omega$  to predict the reactivity of these processes.<sup>12</sup>

The mechanism of the DA reaction between **Cp** and **1CN** has been the subject of several theoretical studies.<sup>8,17,18</sup> This cycloaddition takes place along an asynchronous one-step mechanism.<sup>17b</sup> The presence of a cyano group in the dienophile decreases the energy barrier with an increase in the rate. In the gas phase, this cycloaddition presents a slight exo selectivity<sup>17</sup> that is changed by the inclusion of solvent effects.<sup>18</sup> Inclusion of a second cyano group on **2CN** decreases more markedly the energy barrier along a more asynchronous TS.<sup>17b</sup> The barriers for the **Cp** + **1CN** and **Cp** + **2CN** cycloadditions obtained at the B3LYP/6-31G\* level, 16.0 and 9.3 kcal/mol, respectively, are closer to the experiment (see Table 1).<sup>17</sup>

We present herein the results of a density functional theory<sup>19,20</sup> (DFT) study on the DA reactions between **Cp** and the complete series of cyano ethylenes reported by Sauer et al.<sup>3</sup> (see Scheme 1). Our purpose is to contribute to a better understanding of the influence of substitution at the C1 and C2 carbon atoms of ethylene (the dienophile) on these polar cycloadditions and the origins of the kinetic outcomes, and to shed some light on the mechanistic details of the concerted polar reactions.

## 2. Model Equations

The global electrophilicity index,  $\omega$ , which measures the stabilization in energy when the system acquires an additional electronic charge,  $\Delta N$ , from the environment, has been given the following simple expression:<sup>13</sup>

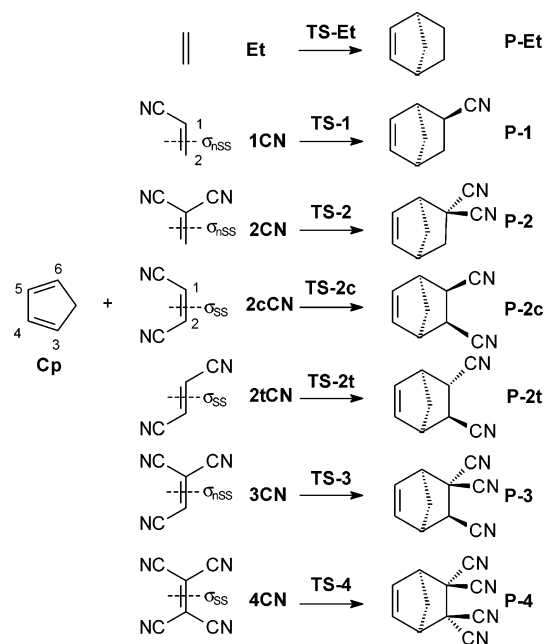
$$\omega = \frac{\mu^2}{2\eta} \quad (1)$$

in terms of the electronic chemical potential  $\mu$  and the chemical hardness  $\eta$ , which may be approached in terms of the one-electron energies of the frontier molecular

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## SCHEME 1



orbital HOMO and LUMO,  $\epsilon_H$  and  $\epsilon_L$ , as  $\mu \approx \epsilon_H + \epsilon_L/2$  and  $\eta \approx \epsilon_L - \epsilon_H$ , respectively.<sup>19,21</sup> The electrophilicity index encompasses both the propensity of the electrophile to acquire an additional electronic charge driven by  $\mu^2$  (the square of the electronegativity) and the resistance of the system to exchange electronic charge with the environment described by  $\eta$ , simultaneously. A good electrophile is in this sense characterized by a high value of  $\mu$  and a low value of  $\eta$ . Associated with the definition of global electrophilicity, there is an additional and useful relationship that accounts for the maximum electronic charge,  $\Delta N_{\max}$ , that the electrophile may accept from the environment. Note that in the present approach, the environment may be represented by either external effects coming for instance from the interaction with the solvent or more simply as *field effects* coming from the presence of substituent groups in the molecule. It has been defined as:<sup>13</sup>

$$\Delta N_{\max} = -\frac{\mu}{\eta} \quad (2)$$

Starting from eq 1 it is possible to define a local (regional) counterpart for the  $\omega$  and  $\Delta N_{\max}$  quantities as follows: use the inverse relationship between chemical hardness and the global softness  $S = 1/\eta$ <sup>19</sup> and the sum rule for  $S$ , namely  $S = \sum_k s_k^+$ <sup>19,21</sup> to rewrite eq 1. There results:

$$\omega = \frac{\mu^2}{2\eta} = \frac{\mu^2}{2} S = \frac{\mu^2}{2} \sum_k s_k^+ = \sum_k \omega_k \quad (3)$$

from which we may define a semilocal, or regional electrophilicity power condensed to atom  $k$  given by:

$$\omega_k = \frac{\mu^2}{2} s_k^+ \quad (4)$$

Also, the following partition for  $\Delta N_{\max}$  is possible in terms

of the electrophilic Fukui function  $f_k^+$ :

$$\Delta N_{\max}(\mathbf{k}) = \Delta N_{\max} f_k^+ \quad (5)$$

Note that within the present model, the maximum electrophilicity power within a molecule will be located at the softest site of the system. If we further use the exact relationship between local softness and electrophilic Fukui function, namely  $s_k^+ = S f_k^+$ ,<sup>19,21</sup> then the local electrophilicity power given in eq 4 may be also expressed as:

$$\omega_k = \frac{\mu^2}{2} s_k^+ = \frac{\mu^2 S}{2} f_k^+ = \omega f_k^+ \quad (6)$$

thereby showing that the maximum electrophilicity power in a molecule will be developed at the site where the Fukui function for a nucleophilic attack  $f_k^+$  displays its maximum value, i.e., at the active site of the electrophile. Local (regional) descriptors of electrophilicity/nucleophilicity have been previously proposed in the literature.<sup>22</sup> The relative electrophilicity ( $s_k^+/s_k^-$ ) and relative nucleophilicity ( $s_k^-/s_k^+$ ) indexes introduced by Roy et al.<sup>22</sup> defined in terms of the electrophilic and nucleophilic softness apply only to those sites having comparable and higher values of  $s_k^+$  and,  $s_k^-$ . In this sense, these definitions are less universal than the one presented in eqs 4 and 6 for local electrophilicity. Another advantage of eqs 4 and 6 is that they provide normalized definitions of local electrophilicity.<sup>23</sup>

### 3. Computational Methods

In recent years, theoretical methods based on the DFT have emerged as an alternative to traditional ab initio methods in the study of structure and reactivity of chemical systems. DA reactions and related cycloadditions have been the object of several DFT studies showing that functionals that include gradient corrections and hybrid functionals, such as B3LYP, together with the 6-31G\* basis set lead to potential energy barriers in good agreement with the experimental results.<sup>24</sup> Therefore, in the present study we have selected the B3LYP<sup>25</sup> exchange-correlation functionals, together with the standard 6-31G\* basis set,<sup>26</sup> for the complete characterization of the potential energy surface (PES) for these cycloadditions. The optimizations were carried out by using the Bery analytical

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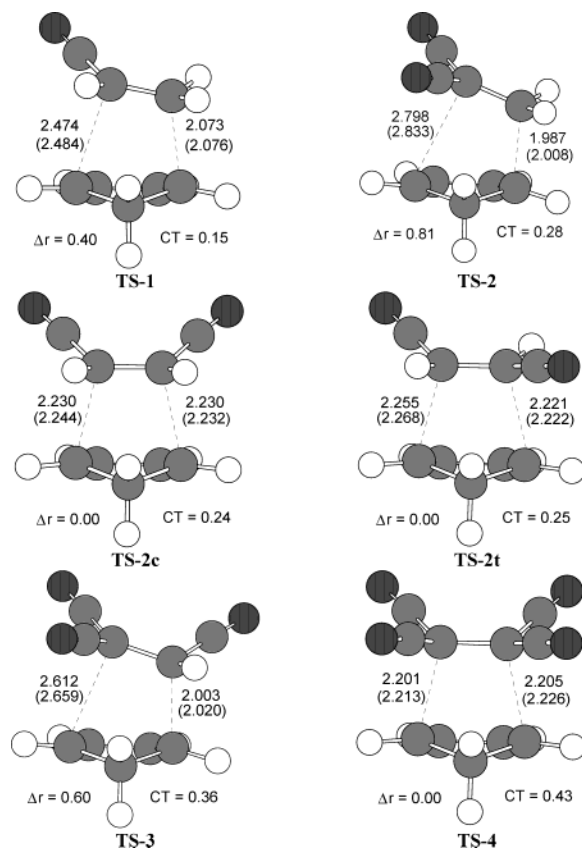
gradient optimization method.<sup>27</sup> The stationary points were characterized by frequency calculations to verify that the transition structures had one and only one imaginary frequency. The intrinsic reaction coordinate (IRC)<sup>28</sup> path was traced to check the energy profiles connecting each transition structure to the two associated minima of the proposed mechanism by using the second-order González–Schlegel integration method.<sup>29</sup> The values of the enthalpies at 20 °C have been calculated based on the total energies and the thermochemical analysis at the B3LYP/6-31G\* level.<sup>26</sup> The thermal contributions to the vibrational energy were scaled by 0.96.<sup>30</sup> The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method.<sup>31</sup> All calculations were carried out with the Gaussian 98 suite of programs.<sup>32</sup>

Solvent effects have been considered in B3LYP/6-31G\* optimizations of the gas-phase stationary points with use of a relatively simple self-consistent reaction field (SCRF) method<sup>33</sup> based on the polarizable continuum model (PCM) of Tomasi's group.<sup>34</sup> The solvent used in the experimental work is dioxane, for which the dielectric constant value is  $\epsilon = 2.22$ . We have used  $\epsilon = 2.247$ , which corresponds to the dielectric constant of benzene.

Electrophilic and nucleophilic Fukui functions<sup>35</sup> condensed to atoms have been evaluated from single-point calculations performed at the ground state of molecules at the same level of theory, using a method described elsewhere.<sup>36</sup> This method evaluates Fukui functions by using the coefficients of the frontier molecular orbitals involved in the reaction and the overlap matrix. The global electrophilicity was evaluated by using eq 1 with the electronic chemical potential and chemical hardness obtained from the one-electron energies of the frontier molecular orbitals, HOMO and LUMO.

#### 4. Results and Discussion

**(a) Energies.** While the cycloadditions of **Cp** with the cyano ethylenes **2CN**, **2tCN**, and **4CN** have a unique reactive channel, those with the cyano ethylenes **1CN**,



**FIGURE 1.** Transition structures corresponding to the cycloadditions between cyclopentadiene and the cyano-substituted ethylenes. The bond lengths directly involved in the reaction and the asynchronicity, i.e.,  $\Delta r = d(\text{C1}-\text{C6}) - d(\text{C2}-\text{C3})$ , are given in angstroms. The charge transfer (CT) is in electron units. The solution phase values are given in parentheses.

**2cCN**, and **3CN** have two reactive channels associated with the endo and exo approach of the cyano groups relative to the  $\pi$  system of **Cp**. In this study we have considered only the endo approach mode. An analysis of the PES for these DA reactions indicates that they correspond to a one-step processes. Therefore, six TSs, **TS-1**, **TS-2**, **TS-2c**, **TS-2t**, **TS-3**, and **TS-4**, and the corresponding cycloadducts have been located and characterized in the PES. The cycloaddition between **Cp** and ethylene (**Et**) also has been studied to compare some relevant parameters. The stationary points corresponding to the cycloaddition reaction between **Cp** and the six cyano ethylenes are presented in Scheme 1, together with the atom numbering. Some selected geometrical parameters of the calculated TSs are shown in Figure 1. Table 2 reports the values of the relative enthalpies of the TSs and cycloadducts. Values of relative entropies and free energies are given in Table 2S (see Supporting Information). The TS associated with the [4+2] cycloaddition between **Cp** + **Et**, **TS-Et**, is shown in Figure 2.

The computed activation enthalpy (AE) for the **Cp** + **Et** cycloaddition,<sup>17</sup> 21.0 kcal/mol, is in closer agreement with the experimental value (21.9 kcal/mol).<sup>17c</sup> An analysis of the relative enthalpies given in Table 2 shows that there is a reduction of the AE with the increase of the EW substitution on ethylene. Inclusion of a cyano group on ethylene (**1CN**) decreases the AE to 17.5 kcal/mol. A

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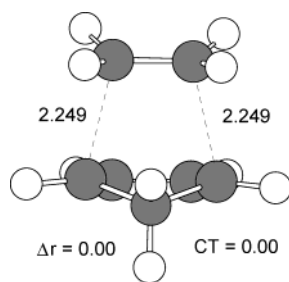
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**TABLE 2.** B3LYP/6-31G\* Relative Enthalpies<sup>a</sup> (kcal/mol) Computed at 20 °C for the Stationary Points Corresponding to the Cycloaddition Reactions of Cyclopentadiene with Ethylene and the Cyano-Substituted Ethylenes, in Vacuo and in Benzene

	in vacuo	in benzene
TS-Et	21.0	
TS-1	17.5	16.7
TS-2	10.5	8.7
TS-2c	16.3	14.5
TS-2t	15.2	14.3
TS-3	11.3	9.0
TS-4	11.5	8.7
P-Et	-20.5	
P-1	-18.4	-18.53
P-2	-16.5	-16.97
P-2c	-16.0	-17.09
P-2t	-16.9	-17.60
P-3	-14.1	-15.34
P-4	-10.7	-12.45

<sup>a</sup> Relative to **Cp** + ethylene derivative.



**FIGURE 2.** Transition structure corresponding with the cycloaddition between cyclopentadiene and ethylene. The bond lengths directly involved in the reaction and the asynchronicity, i.e.,  $\Delta r = d(\text{C1}-\text{C6}) - d(\text{C2}-\text{C3})$ , are given in angstroms. The charge transfer (CT) is in electron units.

more drastic effect is found with the inclusion of a second cyano group at the same C1 carbon atom, which yields the nonsymmetrically substituted (nSS) **2CN**. This reaction, with an AE value of 10.5 kcal/mol, presents the largest reduction of the AE induced by substitution, in agreement with the relative rates given in Table 1. A different behavior is found for the C1 and C2 symmetrically substituted (SS) ethylenes **2cCN** and **2tCN**, which present AEs slightly lower than that found for **1CN**, namely 16.3 and 15.2 kcal/mol, respectively. For acrylonitrile and the disubstituted cyanoethylenes the experimental trends in activation energies given in Table 1 are predicted by the DFT calculations. Finally, the tri- and tetrasubstituted derivatives **3CN** and **4CN** present also very low AEs (ca. 11 kcal/mol). However, these barriers are larger than those expected from the relative rates given in Table 1. The activation entropies for the cycloadditions of the cyanoethylene series, in the range of -45 to -48 cal/(mol·K), are closer to that computed for the **Cp** + **Et** cycloaddition, -43 cal/(mol·K). These negative entropies raise the activation free energies between 13 and 14 kcal/mol over the activation enthalpy values given in Table 1 (see Table 2S in the Supporting Information). These cycloadditions are exothermic processes by -11 and -20 kcal/mol. Increasing substitution on ethylene results in a decrease in the exothermic character of the process.

**(b) Geometries.** The lengths of the C2-C3 and C1-C6 forming bonds at the TSs are 2.073 and 2.474 Å (at

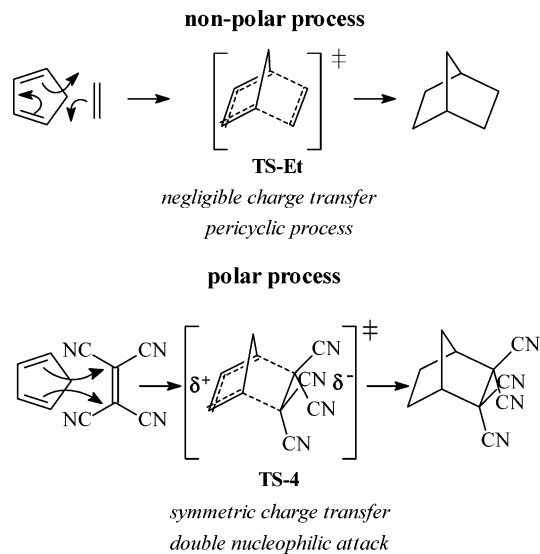
**TS-1**), 1.987 and 2.798 Å (at **TS-2**), 2.230 and 2.230 Å (at **TS-2c**), 2.221 and 2.255 Å (at **TS-2t**), 2.003 and 2.612 Å (at **TS-3**), and 2.201 and 2.205 Å (at **TS-4**), respectively. The extent of the asynchronicity can be measured by means of the difference between the distances of the two  $\sigma$ -bonds that are being formed in the reaction, i.e.,  $\Delta r = d(\text{C1}-\text{C6}) - d(\text{C2}-\text{C3})$ . The asynchronicity at the TSs is 0.40 at **TS-1**, 0.81 at **TS-2**, 0.00 at **TS-2c**, 0.03 at **TS-2t**, 0.61 at **TS-3**, and 0.00 at **TS-4**. Therefore, while the nSS **1CN**, **2CN**, and **3CN** present asynchronous TSs, **TS-1**, **TS-2**, and **TS-3**, the SS ethylenes **2cCN**, **2tCN**, and **4CN** present synchronous TSs, **TS-2c**, **TS-2t**, and **TS-4**, respectively. Despite the high asynchronicity found at **TS-2**, the IRC analysis asserts the one-step nature of these cycloadditions. For the **Cp** + **Et** cycloaddition the lengths of the C2-C3 and C1-C6 forming bonds at **TS-Et** are 2.249 Å (see Figure 2).<sup>17</sup> The asynchronicity at this TS,  $\Delta r = 0.00$ , indicates that it corresponds to a synchronous concerted bond-formation process.

The analysis of the energetic and geometrical results allows us to anticipate some important conclusions for this series of related DA reactions. For instance: (i) the SS ethylenes afford synchronous TSs; (ii) the symmetric arrangement on the C1 and C2 carbon atoms of ethylene markedly decreases the effectiveness of the substitution (the cycloaddition for **2CN** is ca. 1000 times faster than those for **2cCN** and **2tCN**); and (iii) the more asynchronous **TS-2** corresponds with the larger reduction on the AE and with the larger increase of the relative rate (see the relative rate between **1CN** and **2CN**, 10 000 times, and that between **2CN** and **3CN**, 10 times, in Table 1).

The C1-C2 bond-lengths at the **P1**, **P2**, **P3**, and **P4** cycloadducts are 1.536, 1.589, 1.606, and 1.635 Å, respectively. There is an increase of the C1-C2 bond length associated with an increase of the cyano substitution on the C1 and C2 carbon atoms. Therefore, the unfavorable interactions that appear between the cyano substituents on the C1 and C2 carbon atoms of **P3** and **P4** can account for the loss of the exothermicity on the formation of the cycloadducts with **P3** and **P4**. This trend that is also observed in the C1-C2 bond lengths at the TSs **TS-1**, **TS-2**, **TS-3**, and **TS-4**, 1.402, 1.416, 1.434, and 1.457 Å, respectively, explains part of the loss of the reduction of AE found in the cycloadditions with **3CN** and **4CN**.

**(c) Charge-Transfer Analysis.** The natural population analysis<sup>31</sup> allows the evaluation of the charge transferred along these polar cycloaddition processes.<sup>10c</sup> The B3LYP/6-31G\* atomic charges have been partitioned between **Cp** and the electron-poor substituted ethylene (see CT in Figure 1).

The negative charge transferred from the donor **Cp** to the cyano ethylenes is 0.15 e at **TS-1**, 0.28 e at **TS-2**, 0.24 e at **TS-2c**, 0.25 e at **TS-2t**, 0.36 e at **TS-3**, and 0.43 e at **TS-4**, thereby indicating that the nature of these TSs may be traced to some zwitterionic character that increases with the EW substitution.<sup>10b</sup> There is a clear correlation between the increase in the rate shown in Table 1 and the charge transfer at the corresponding TS. Thus, the most substituted tetracyano derivative **4CN**, which corresponds with the faster cycloaddition of the series, presents the largest charge transfer at the TS, 0.4 e. This is the more polar process of this series. However, **TS-4** corresponds with a synchronous bond-formation process. On the other hand, for the disubstituted ethylenes, **2-CN**, **2c-CN**, and **2t-CN**, the **TS-2** that corre-

**SCHEME 2. Synchronous Concerted Mechanisms for the Diels–Alder Reactions**


sponds to the most asynchronous TS has a larger charge transfer than the **TS-2c** and **TS-2t**. Finally, the concerted TS associated with the **Cp** + **Et** cycloaddition has a negligible charge transfer, ca. 0.0 e, which is consistent with a [4+2] process. This good correlation allows us to propose that the feasibility of a DA reaction is mainly related to the polar character of the process,<sup>14</sup> described by the charge transfer at the corresponding TS.

At this point, we would ask the following question: Are the synchronous **TS-2c**, **TS-2t**, and **TS-4** associated to the [4+2] process? Before we answer this question let us make two meaningful considerations: (1) The computed AE for the **Cp** + **4CN** reaction is ca. 10 kcal/mol lower than that for the **Cp** + **Et** one, which corresponds to a [4+2] process. Experimental data show that the **Cp** + **4CN** reaction is 10<sup>12</sup> faster than the **Cp** + **Et** one (see Table 1). (2) While the TS associated to the **Cp** + **4CN** reaction (**TS-4**) presents the largest charge transfer of the series, the TS for the **Cp** + **Et** one (**TS-Et**) presents a negligible charge transfer, which is consistent with a nonpolar process. Therefore, although these DA reactions present synchronous TSs with a similar bond-formation extent, they are associated to processes of different electronic nature: thus, while the **Cp** + **Et** reaction corresponds to a nonpolar [4+2] cycloaddition associated to the pericyclic process,<sup>37</sup> the **Cp** + **4CN** reaction is associated to a polar reaction where the C3 and C6 carbon atoms of the **Cp** (the more nucleophilic centers) concurrently attack the two more electrophilic centers of the symmetric **4CN** (i.e. the C1 and C2 atoms). A schematic representation of the behaviors for these synchronous concerted DA reactions is given in Scheme 2. Therefore, we may conclude that the synchronicity based on the extent of the bond formation only is not a definitive pattern to classify a DA reaction as a pericyclic or a polar process.

**(d) Solvent Effects.** Solvent effects on cycloaddition reactions are well-known and have received considerable attention, especially in the past few years. As solvent can

**TABLE 3. Global Properties<sup>a</sup> of Cp, Et, and the Six Cyano-Substituted Ethylenes**

	HOMO	LUMO	$\mu$	$\eta$	$\omega$	$\Delta N_{\max}$
<b>4CN</b>	-0.3351	-0.1823	-0.2587	0.1528	5.96	1.69
<b>3CN</b>	-0.3231	-0.1497	-0.2364	0.1734	4.38	1.36
<b>2tCN</b>	-0.3068	-0.1126	-0.2097	0.1942	3.08	1.08
<b>2cCN</b>	-0.3056	-0.1101	-0.2078	0.1956	3.01	1.06
<b>2CN</b>	-0.3112	-0.1037	-0.2074	0.2075	2.82	1.00
<b>1CN</b>	-0.2892	-0.0563	-0.1728	0.2329	1.74	0.74
<b>Cp</b>	-0.2115	-0.0099	-0.1107	0.2016	0.83	0.55
<b>Et</b>	-0.2667	0.0188	-0.1239	0.2855	0.73	0.43

<sup>a</sup> Electronic chemical potential,  $\mu$ , and chemical hardness,  $\eta$ , values are in au; electrophilicity power values,  $\omega$ , are in eV.

modify both activation energy and geometries, their effects on the reaction can give useful information about the mechanism. As a consequence, solvent effects have been evaluated by geometrical optimization on the gas-phase B3LYP/6-31G\* geometries with use of a relatively simple SCRF method<sup>33</sup> based on the PCM method of Tomasi's group.<sup>34</sup> Table 2 reports the relative enthalpies of the optimized stationary points obtained by the SCRF method, while some selected geometrical parameter are given in Figure 1.

Inclusion of solvent effects stabilizes more efficiently the TSs than reactants because of the zwitterionic character of the former. As a consequence, with the inclusion of solvent effects there is a decrease of the AE that is enhanced with the increase of the substitution on ethylene, between 0.8 and 2.8 kcal/mol. With the inclusion of solvent effects the AEs for **TS-1** and **TS-2**, 16.7 and 8.7 kcal/mol, respectively, are closer to the experimental activation energies given in Table 1, while those for **TS-2c** and **TS-2t**, 14.5 and 14.3 kcal/mol, respectively, are slightly larger. Finally, **TS-3** and **TS-4** undergo the largest reduction because of the large zwitterionic character of these TSs.

A comparison of the geometrical parameters of the TSs given in Figure 1 shows that inclusion of solvent effects on the geometry optimization does not modify substantially the gas-phase geometries.<sup>12c</sup> Therefore, the synchronicities found in the gas phase remain with the inclusion of solvent effects. The length of the forming bonds obtained in the gas phase is 0.05 Å shorter than those obtained with the SCRF method. Thus, the stabilization of the TSs by the inclusion of solvent effects leads to earlier TSs.<sup>12c</sup> Finally, the inclusion of solvent effects does not modify the symmetric **TS-2c**, **TS-2t**, and **TS-4**. Therefore, the analysis made in the gas phase for this series of DA reactions is also valid in the solution phase.

**(e) Global and Local Electrophilicity/Nucleophilicity Analysis.** These cycloaddition reactions also have been analyzed by using the global and local indexes defined in the context of the DFT. Recent studies carried out on cycloaddition reactions with a polar character have shown that these indexes are powerful tools to study both reactivity<sup>12,14</sup> and regioselectivity.<sup>16</sup> In Table 3 the static global properties, electronic chemical potential  $\mu$ , chemical hardness  $\eta$ , and global electrophilicity  $\omega$ , defined in eq 1, for **Cp**, **Et**, and the six cyano ethylenes are displayed, while the local properties are presented in Table 4.

The electronic chemical potentials of cyano ethylenes ranging from -0.1728 to -0.2587 au are less than the electronic chemical potential of **Cp** ( $\mu = -0.1107$  au),

(37) R. B. Woodward and R. Hoffmann defined the concept of a pericyclic reaction as: "a concerted reaction in which all bonds are made or broken around a circle."<sup>2b,5b</sup>

**TABLE 4. Local Properties of Et and the Six Substituted Ethylenes.**

	$f_1^+$	$\omega_1$	$\Delta N_{\max 1}$	$f_2^+$	$\omega_2$	$\Delta N_{\max 2}$
<b>Et</b>	0.5000	0.37	0.22	0.5000	0.37	0.22
<b>1CN</b>	0.2657	0.46	0.20	0.4686	0.82	0.35
<b>2CN</b>	0.2087	0.59	0.21	0.4989	1.41	0.50
<b>2tCN</b>	0.2998	0.92	0.32	0.2998	0.92	0.32
<b>2cCN</b>	0.3058	0.92	0.33	0.3058	0.92	0.33
<b>3CN</b>	0.2359	1.03	0.32	0.3331	1.46	0.45
<b>4CN</b>	0.2570	1.53	0.44	0.2570	1.53	0.44

thereby indicating that the net charge transfer will take place from **Cp** toward these electron-poor ethylenes. In addition, for the **1CN**, **2CN**, **3CN**, and **4CN** subseries there is a good correlation between the substitution pattern on the ethylene, the increase of the negative electronic chemical potential value, and the charge transfer found at the corresponding TS. For the **2CN**, **2tCN**, and **2cCN** subseries the correlation is lost because of the symmetry present in **2cCN** and **2tCN** (see later).

The electrophilicity of this series of cyano ethylenes, which have  $\omega$  values between 1.74 and 5.96 eV, also increases with the substitution. Therefore, for the **1CN**, **2CN**, **3CN**, and **4CN** subseries the difference in electrophilicity between the diene and dienophile,  $\Delta\omega$ , which has been proposed as a measure of the polar character of the DA reaction,<sup>14</sup> is also in agreement with the increase of the polar character of the cycloaddition process deduced from the charge-transfer analysis. On the other hand, the very low value of  $\Delta\omega$  for the **Cp** + **Et** DA reaction ( $\Delta\omega = 0.1$  eV) agrees well with a nonpolar process associated to a pericyclic TS.<sup>14</sup>

The local (regional) electrophilicity,  $\omega_k$ , that has been used to elucidate the regioselectivity of polar DA reactions<sup>16</sup> can be used as a measure of the distribution of the global electrophilicity in the different atomic sites of a molecule (see for instance eq 6). An analysis of the local electrophilicity index for the nSS ethylenes **1CN**, **2CN**, and **3CN** shows that the most electrophilic center of the molecule corresponds to the less substituted C2 carbon atom of the ethylene (the  $\beta$  position). However, the SS ethylenes **2cCN**, **2tCN**, and **4CN** present electrophilic activation at the C1 and C2 centers. The nSS **2CN** presents a larger electrophilic activation at the C2 center,  $\omega_k = 1.41$  eV, when it is compared to that of the SS **4CN**, at the same center. The local electrophilicity value is brought to  $\omega_k = 1.53$  eV. In addition, the  $\Delta N_{\max}(k)$  index defined in eq 5 at the C2 center in the nSS **2CN** is even larger than that of the SS **4CN**, the most electrophilic ethylene of the present series. Note that the  $\Delta N_{\max}(k)$  at the C2 center of **2CN**, 0.50 e, is larger than the actual charge transfer found at the **TS-2**, 0.28 e. These results allow us to explain the synchronicity on the bond-formation at this polar DA reaction using SS ethylenes. Although the SS **4CN** is the most electrophilic reagent of this series, with a  $\Delta N_{\max}$  value of 1.69 e, the  $\Delta N_{\max}(k)$  of the symmetric C1 and C2 centers, 0.44 e, represents ca. 25% of the charge capacity  $\Delta N_{\max}$  of the molecule. A different behavior is found for the nSS **2CN** where  $\Delta N_{\max}(k)$  at the C2 center, 0.50 e, represents 50% of the global charge capacity of the molecule, 1.00 e. Therefore, the SS **4CN** prefers the simultaneous nucleophilic attack at the electrophilic C1 and C2 centers to perform a larger charge-transfer process at the corresponding TS. A similar analysis can be performed on the SS **2cCN** and

**2tCN** reagents, which also prefer the synchronous bond-formation through a simultaneous nucleophilic attack of the C3 and C6 centers of the symmetric **Cp**.

This analysis, which can be extrapolated to other polar cycloaddition reactions using **Cp** and SS ethylenes as maleic anhydride,<sup>38</sup> provides a reasonable explanation about the synchronicity of these polar bond-formation processes. Note that the SS maleic anhydride has an electrophilicity value,  $\omega = 3.24$  eV,<sup>14</sup> that is larger than that for the dicyano-substituted ethylenes.

## 5. Concluding Remarks

The transition structures for a series of Diels–Alder reactions between cyclopentadiene and mono-, di-, tri-, and tetracyanoethylene derivatives have been studied with use of DFT methods. These polar cycloadditions can be considered as the nucleophilic attack of cyclopentadiene to the electron-poor substituted ethylene. The increase of the EW substitution on ethylene (the electrophile) increases the rate of these polar cycloadditions. However, the symmetric arrangement of the substituents on the *cis*- and *trans*-1,2-di- and tetracyanoethylene decreases the effectiveness of the substitution. The analysis of the geometries of the TSs associated to the cycloaddition of these SS ethylenes shows that they correspond to synchronous bond-formation processes. The very low AE computed for the reaction with tetracyanoethylene together with the large charge transfer found at the corresponding TS indicate that these processes are associated to polar cycloadditions, where **Cp** and the SS ethylene act as nucleophile and electrophile, respectively, instead of a dienophile/diene pair in a [4+2] process. An analysis of the global electrophilicity of this series of cyano ethylenes points out the increase of the electrophilic character of the cyano ethylene with increasing substitution. Finally, an analysis of the local electrophilicity for the SS ethylenes allows us to explain the synchronicity on the bond-formation of these cycloadditions, as a consequence of the symmetric distribution of the global electrophilicity on the C1 and C2 electrophilic carbon atoms of the SS ethylene.

**Acknowledgment.** This work received partial financial support from the Ministerio de Educación y Cultura of the Spanish Government by DGICYT (projects PB98-1429 and BQU2002-01032) and Fondecyt (Grant No. 1020069). L.R.D. thanks the Fondecyt (Grant No. 7020069) for financial support and Universidad Andrés Bello and Universidad de Chile for the warm hospitality.

**Supporting Information Available:** Tables giving the total energies, and relative enthalpies, entropies, and free energies for the stationary points corresponding to the cycloaddition reactions of **Cp** with ethylene and the cyano-substituted ethylenes; the B3LYP/6-31G\* computed total energies, unique frequency imaginary and Cartesian coordinates of the transition structures corresponding to the cycloadditions between cyclopentadiene and the cyano-substituted ethylenes, **TS-1**, **TS-2**, **TS-2c**, **TS-2t**, **TS-3**, and **TS-4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO020714N

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