A DFT Characterization of the Mechanism for the Cycloaddition Reaction between 2-Methylfuran and Acetylenedicarboxylic Acid

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The molecular mechanism for the cycloaddition reaction between 2-methylfuran and acetylenedicarboxylic acid (ADA) has been characterized using density functional theory methods at the B3LYP/6-31+G* theory level. An analysis of the results on the reaction pathway shows that the reaction takes place along a stepwise mechanism. The initial step corresponds to the nucleophilic attack of the C5 position of the furan ring to one carbon atom of the conjugated acetylenic system of ADA to give a zwitterionic intermediate. Closure of this intermediate along the nucleophilic attack of the other acetylenic carbon to the substituted C2 position of the furan ring affords the Diels−Alder cycloadduct. Although the B3LYP/6-31G* calculations afford good potential energy barriers, the inclusion of diffuse functions is required in order to obtain a complete characterization of the molecular mechanism.

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.[1] 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 σ-bonds are formed at the expense of two π-bonds in the starting material.[2]

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 structures can be built. However, not all possibilities take place easily. While the DA reaction between unsubstituted dienes and dienophiles demands high temperatures, the presence of electron-releasing substituents in the diene and electron-withdrawing in the dienophile, or vice versa, can drastically accelerate the reaction.

The mechanism of the DA reaction has been controversial for some time.[3] The archetypal DA reaction of butadiene and ethylene[4] is exothermic by 40 kcal/mol and has a reaction barrier of 27.5 kcal/mol. It may occur via either a synchronous concerted mechanism or a stepwise mechanism involving the formation of diradical intermediates.[3] 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 for the reaction to be reasonably fast. Furthermore, this type of substitution on diene and dienophile favors an asynchronous concerted mechanism.

Several computational ab initio studies on this mechanism type have recently been published.[5] Sustmann et al.[6] have studied the DA reactions of (*E*)-1-(dimethylamino)-1,3-butadiene with various dienophiles. Their results indicate that the reaction mechanism changes progressively from an asynchronous concerted pathway to a stepwise one with the increasing ability of the dienophile to stabilize a negative charge. Under suitable conditions, the intermediate of the stepwise process was trapped.[7] It is precisely the mechanism of these cycloadditions which interests us.[8]

Five-membered heterocycle systems, such as pyrrole and furan, have been used as dienes with electron-poor acetylenes as dienophiles in [4+2] cycloaddition reactions.[1a] Recently, we have reported several theoretical studies devoted to these cycloaddition reactions (see Scheme 1).[9−12] These studies point out that the mechanism changes from concerted to stepwise with the increase of the nucleophilic and electrophilic character of the diene and dienophile, respectively. However, while HF/6-31G* calculations allow a complete characterization of potential energy surface (PES) for the stepwise mechanism, density functional theory (DFT) studies at the B3LYP/6-31G* calculation level allow only the characterization of one transition structure (TS).

Thus, while the [4+2] intermolecular cycloaddition reaction of the hexafluorobut-2-yne **1** with a pyrrole ring of *N*,*N'*-dipyrrolylmethane **4** takes place along a synchronous concerted mechanism,[9] **TS−I** (see Figure 1), the cycloaddition reaction between dimethyl acetylenedicarboxylate **2** and 1-methylpyrrole **5**, takes place along a stepwise mechanism.[10] However, B3LYP/6-31G* calculations allow us only to characterize the **TS−II** corresponding to the first step of the stepwise mechanism, since calculations at this level afford a very flat PES around the two TSs and intermediate. This stepwise process can be considered as a nucleophilic attack of the C2 position of the pyrrole ring to a conjugated position of the acetylenic system of **2**, with formation of a zwitterionic intermediate.[10] The larger capacity of **2** relative to **1** to delocalize a negative charge changes the mechanism from concerted to stepwise.[10]

Very recently, we have studied the cycloaddition reaction of **2** with the furan ring of a naphthalenofuranophane **6**.[11] For this reaction, the B3LYP/6-31G* calculations afford a one-step mechanism through the asynchronous concerted **TS−III** (see Figure 1). The oxygen atom of the furan is more electronegative than the nitrogen atom of pyrrole and favors a concerted pathway rather than a stepwise mechanism for the cycloaddition with **2**. On the other hand, for the reaction between the acetylenedicarboxylic acid **3** and one of the furan rings of 1,3-bis(2-furyl)propane **7**, B3LYP/6-31G* calculations give only

SCHEME 1

dienophiles

$E-C\equiv C-E$

1 $E = CF_3$
2 $E = CO_2CH_3$
3 $E = CO_2H$
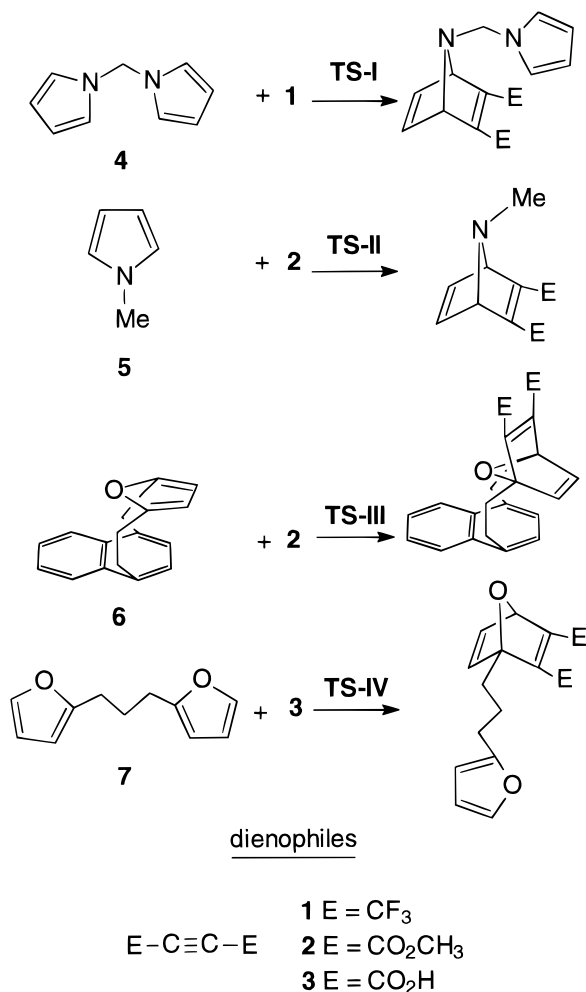
one very asynchronous **TS−IV**.[12] Although the geometrical parameters for **TS−IV** are similar to those for **TS−II**, which corresponds to the first step of stepwise mechanism, an analysis of the corresponding transition vector allows us to associate the **TS−IV** to the second step of the stepwise mechanism, because the main component of the transition vector corresponds to the long forming bond. Again we found that B3LYP/6-31G* calculations do not allow a complete characterization for the stepwise mechanism of this sort of cycloaddition reactions.

In the present paper the stepwise mechanism for the cycloaddition between 2-methylfuran, **8**, and acetylenedicarboxylic acid, **3**, has been studied (see Scheme 2).[13] The purpose of this study is to carry out a complete characterization of the corresponding stationary points, TSs and intermediate, for the stepwise mechanism of these particular cycloaddition reactions using DFT computational methods.
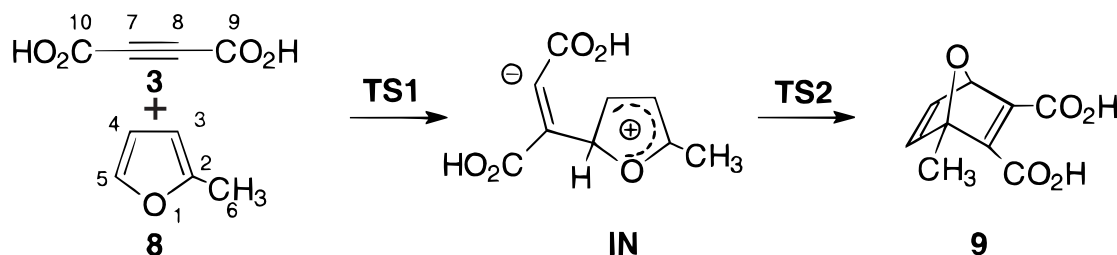
Computing Methods

In recent years theoretical methods based on the DFT methods[14] have emerged as alternatives to traditional ab initio methods in the study of structure and reactivity of chemical systems. Diels−Alder reactions and related cycloaddition reactions have been the object of several density functional studies showing that functionals that include gradient corrections and a hybrid functional, such as B3LYP,[15] together with the 6-31G* basis set,[16] lead to potential energy barriers (PEBs) in good agreement with the experimental results.[8c,9,17] Thus, in the present study geometrical optimizations of the stationary points along the PES were carried out using the gradient corrected functional of Becke, and Lee, Yang, and Parr (B3LYP)[15] for exchange and correlation. Since it was expected that some negative charge can be localized in any stationary points, the 6-31+G* basis set[16] has been used because of its superior ability to accommodate negative charges. The stationary points were characterized by frequency calculations in order to verify that minima and transition structures have zero and one imaginary frequency, respectively. The optimizations were carried out using the Berny analytical gradient optimization method.[18] Several conformations related to the rotation around the single bonds involving the carboxylic acid groups have been considered, and those presented correspond to the most stable conformations. All calculations were carried out with the *Gaussian 94* suite of programs.[19] Optimized geometries of all the structures are available from the authors. The transition vectors,[20] i.e., the eigenvector associated to the unique negative eigenvalue of the force constants matrix, have been characterized. The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method.[21]

Results and Discussion

The stationary points corresponding to the reaction between **3** and **8** have been presented in Scheme 2 together with the atom numbering. The total and relative energies are summarized in Table 1. A schematic representation of the energy profile with the location of the stationary points is depicted in Figure 2, while the geometries of the TSs and intermediate are presented in Figure 3.

Energies. A B3LYP/6-31G* exhaustive exploration of the PES for the cycloaddition reaction between **3** and **8** allows us to find the reactants, **3**+**8**, only one TS, and the final cycloadduct **9**. However, the inclusion of diffuse functions at the B3LYP/6-31+G* level allows the location of the different stationary points for the stepwise mechanism, **3**, **8**, **TS1**, **IN**, **TS2**, and **9**.

All analyses carried out for the unique TS found at the B3LYP/6-31G* level confirm that it corresponds to the **TS2** obtained with the inclusion of diffuse functions. The PEB associated with the **TS2** at the B3LYP/6-31G* level (13.8 kcal/mol) is very similar to that obtained at B3LYP/6-31+G* level, the latter being ca. 0.9 kcal/mol higher than the former. This energetic increase with the inclusion of diffuse functions can
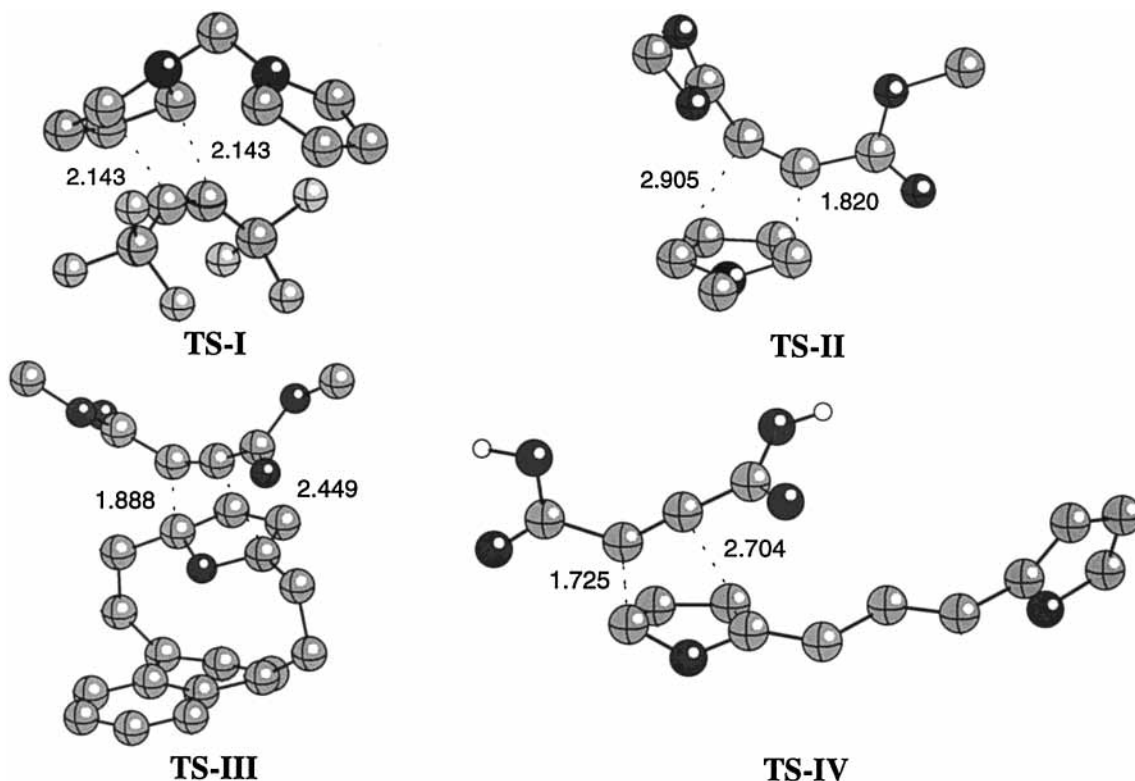
SCHEME 2

2-Methylfuran/ADA Cycloaddition Reaction

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Figure 1. B3LYP/6-31G* transition structures corresponding to the cycloaddition reaction between **1** and **4**, **TS−I**, **2** and **5**, **TS−II**, **2** and **6**, **TS−III**, and **3** and **7**, **TS−IV**. The lengths of the C−C forming bonds involved in the reaction are given in angstroms.

TABLE 1: Total Energies (a.u.) and Relative Energies (kcal/mol, in parentheses) for the Stationary Points of the Cycloaddition Reaction between 3 and 8

	B3LYP/6-31G*		B3LYP/6-31+G*	
3	−454.459608		−454.485157	
8	−269.343715		−269.355163	
TS1			−723.816901	(14.7)
IN			−723.817136	(14.5)
TS2	−723.781347	(13.8)	−723.816920	(14.7)
9	−723.832904	(−18.6)	−723.865647	(−15.9)

be due to a decrease of the basis set superposition error on TSs and intermediate, which decreases with the use of larger basis set.[22] All discussion in the text will be referenced to the B3LYP/6-31+G* results.

The transition structure **TS1** corresponds to the nucleophilic attack of the C5 position of the furan ring to one carbon atom of the conjugated acetylenic system of **3** to give the zwitterionic intermediate **IN**. The presence of the oxygen atom on the furan ring increases the nucleophilic character of the dienic system due to a stabilization of the positive charge that is developing along the charge transfer process, while the presence of two electron-withdrawing carboxyl groups on the acetylenic system facilitates the delocalization of negative charge, allowing ADA to act as an electrophile. Moreover, the presence of the donor methyl group on the C2 position of the furan ring favors and orients the electrophilic attack of **3** to the C5 position of **8**. The PEB associated with **TS1** is 14.7 kcal/mol.

The intermediate **IN** is very unstable and can undergo two transformations. Along **TS1**, the fragmentation of **IN** affords the reactants, while the nucleophilic attack of the anionic C8 center of the intermediate **IN** on the C2 position of the furan ring gives the cycloadduct **9**, via **TS2**, with an imperceptible barrier. This process is very exothermic (−15.9 kcal/mol), the closure attack being an irreversible process. Due to that **TS1**, **IN** and **TS2** are energetic and geometrically related, the attack
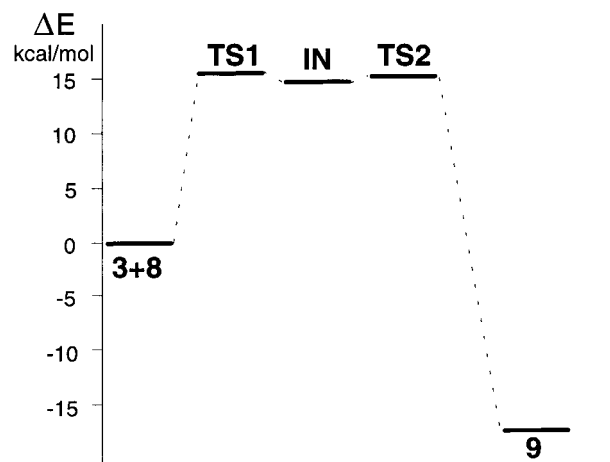

Figure 2. Schematic representation of the B3LYP/6-31+G* energy profile for the cycloaddition reaction between **3** and **8**.

of **3** to **8** along **TS1** affords directly the cycloadduct **9**, without isolation of intermediate **IN**.

Geometries. The length of the C5−C7 forming bond in **TS1** is 1.845 Å, while the distance between the C2 and C8 atoms is 3.020 Å, indicating that these atoms do not bond in this step. In this TS, the carboxyl group at C7 is in the plane of the C7−C8 double bond being formed, whereas the carboxyl group at C8 is perpendicular. This arrangement, which is also present in **IN**, allows an effective delocalization of the negative charge that is being formed at C8.[10] The values of the C8−C7−C10 and C7−C8−C9 bond angles in **TS1** are 130.8° and 166.4°, respectively. These bond angles show that there is a change of hybridization at C7 and C8 as they go from reactants to intermediate.

For the zwitterionic intermediate **IN** the C5−C7 bond length (1.716 Å) is shorter than for **TS1**, while the C2−C8 distance presents a similar value, indicating that these atoms are not
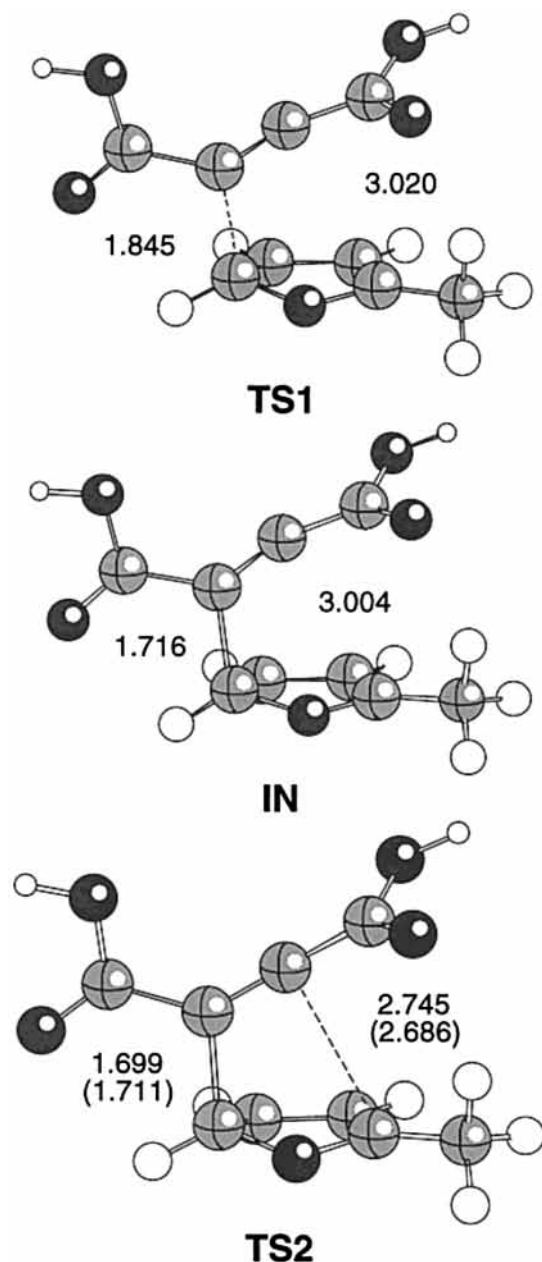
Figure 3. Selected geometrical parameters for the transition structures and intermediate corresponding to the cycloaddition reaction between **3** and **8**. The lengths of the C—C forming bonds involved in the reaction obtained at the B3LYP/6-31+G* and B3LYP/6-31G* (in parentheses) levels are given in angstroms.

bonded. Despite the large C5—C7 bond length found in the intermediate **IN**, it is similar to that found in related intermediates,[10] and it is not surprising if we considered that it is a very unstable species. The O1—C2 bond length (1.336 Å) is shorter than the O1—C5 length (1.414 Å). This fact is due to the π delocalization of the lone pair of the O1 oxygen atom in the C2—C3—C4 allylic system, which allows a stabilization of the positive charge that is developed in this intermediate. The value of the C7—C8—C9 bond angle, 163.2°, together with the NBO analysis of the hybridization states of the orbitals used for bonding at the C8 carbon atom indicate that this atom has an sp hybridization similar to that present in the acetylenic system of **3**. Moreover, this NBO analysis shows also that the C8 atom has a nonbonded p atomic orbital which allows the localization of the charge transferred to the acetylenic system.

The length of the C5—C7 bond in **TS2** is 1.699 Å, while the length of the C2—C8 forming bond is 2.745 Å. These geometrical parameters are closer to those of the unique TS found at the B3LYP/6-31G* level (see Figure 3). This fact together with the rest of analyses (frequency analysis, transition vector, and bond orders) allow us to assert that both TSs correspond to the same chemical process. Moreover, these data are similar to those found for **TS—IV** (see Figure 1), corresponding to the unique TS found at the B3LYP/6-31G* level for the intermolecular cycloaddition between **3** and **7** (see Introduction).

Transition Vector Analysis. The transition vector analyses allow us to understand the chemical process associated with each one of the TSs found along the stepwise reaction pathway. In Table 2 the imaginary frequency and the main transition vector components and their corresponding geometrical parameters are reported for the two TSs.

The main component of the transition vector for **TS1** is associated with the C5—C7 forming bond (0.90). For this TS several components associated with bond angles and dihedral angles also have a participation in the transition vector. These components are associated with the change of hybridization of the C5 and C7 centers along the bond formation process. The component associated with the C2—C8 distance has a quite low value in **TS1** (0.10). This low value, together with the non participation of the C2 and C8 atoms in the corresponding imaginary frequency, can account for a favorable electronic interaction that appears between the neighboring C2 and C8 centers,[8c,10] instead of a bond formation process.

The main component of the transition vector for **TS2** is associated with the C2—C8 forming bond (0.77). The component associated with the C5—C7 bond presents a low value (0.11) because this bond is completely formed along the second step. For this TS several bond angles and dihedral angles participate also in the transition vector (see Table 2). These components are associated with the change of hybridization of the C2 and C8 centers along the C2—C8 bond formation. Thus, the large value found at the C2—C8—C9 bond angle (−0.38) accounts for the change of hybridization that takes place in C8 along the bond formation process. Finally, the components corresponding to the dihedral angles associated with the hydrogen atoms of the C2 methyl group also have a participation in the transition vector for **TS2**. This fact is due to the twist of the methyl group that is taking place to go from **IN** to **9**. In the intermediate **IN** it adopts a bisected conformation (see Figure 3), which allows a hyperconjugative stabilization of the positive charge developed in the furan ring, while in the adduct **9** it adopts an anti conformation relative to the C2—C8 bond formed. This hyperconjugative effect is in agreement with the shortened C2—C6 bond in **IN** (1.478 Å), relative to that in **8** and **9** (1.489 and 1.511 Å, respectively).

The unique imaginary frequencies for **TS1** and **TS2** have the values 229i and 71i cm⁻¹, respectively. These low values indicate that these TSs are associated with the motion of heavy atoms. Moreover, the very low imaginary frequency found for **TS2** is related to the very small PEB associated with nucleophilic attack of the C8 position of the acetylene residue to the C2 position of the furan.

The non synchronicity in the bond formation process along the stepwise mechanism is also shown by the fact that the imaginary frequency of **TS1** is mainly associated with the motion of the C5 and C7 atoms along the C5—C7 forming bond, while for **TS2** it is associated with the motion of the C2 and C8 atoms along the C2—C8 forming bond.

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TABLE 2: B3LYP/6-31+G* Imaginary Frequency (cm^{-1}), Hessian Unique Negative Eigenvalue (a. u.), Main Components of the Transition Vector C (a.u.), and Corresponding Geometric Parameters G (bonds in Å, angles in degrees) for the Transition Structures TS1 and TS2

	TS1			TS2	
imag. freq.		229.3i			70.7i
Eigenvalue		−0.0147			−0.0044
	C	**G**		**C**	**G**
C2−C8	0.104	3.020	C2−C8	0.769	2.745
C5−C7	0.902	1.845	C5−C7	0.114	1.699
O1−C5	−0.095	1.398	C2−C8−C9	−0.379	94.5
O1−C5−C7	−0.120	101.9	C6−C2−C3−O1	0.180	170.3
C5−C7−C10	−0.132	106.7	C8−C2−C3−O1	0.185	−73.6
C5−O1−C2−C3	0.148	−13.3	C5−O1−C2−C3	0.172	−21.1
H5−C5−O1−C2	0.246	159.0	C7−C5−O1−C2	−0.173	−84.5
			H5−C5−O1−C2	−0.115	160.0
			O1−C2−C6−H6	−0.116	115.5
			O1−C2−C6−H6	−0.125	−126.1
			O1−C2−C6−H6	−0.139	−75.5

TABLE 3: Wiberg Bond Orders at the Transition Structures and Intermediate Corresponding to the Stepwise Cycloaddition Reaction between 3 and 8

	TS1	IN	TS2
O1−C2	1.10	1.12	1.11
C2−C3	1.40	1.35	1.32
C3−C4	1.47	1.52	1.56
C4−C5	1.24	1.17	1.15
O1−C5	0.94	0.91	0.91
C2−C8	0.10	0.12	0.17
C5−C7	0.55	0.69	0.72
C7−C8	2.24	2.04	2.02
C7−C10	1.02	1.01	1.01
C8−C9	1.20	1.25	1.23

Bond Orders and Charge Analysis. A more balanced measure of the extent of bond formation along the reaction pathway is provided by the concept of bond order (BO). This theoretical tool has been used to study the molecular mechanism of chemical reactions. To follow the nature of this process, the Wiberg bond indices[23] have been computed. The results are included in Table 3.

For **TS1** the value of the BO for the C5−C7 forming bond is 0.55, while the value of the BO between the C2 and C8 atoms is 0.10. These data are in agreement with the C5−C7 bond formation. The quite low value of BO between the C2 and C8 atoms in **TS1** is a consequence of the arrangement of the C8 center relative to the C2 position of the furan ring, and it is not indicative of a bond formation process.[8c,10] The value of the C7−C8 BO in **TS1** (2.24) shows the double bond formation from the triple bond present in **3**. The slightly larger value for the O1−C2 BO (1.10) than for the O1−C5 one (0.94) in **TS1** accounts for a slight π character of the O1−C2 single bond due to the delocalization of the lone pair of the O1 oxygen atom on the C2−C3−C4 allylic system. Moreover, the slightly larger value for the C8−C9 BO (1.20) than for the C7−C10 one (1.02) in **TS1** accounts for a slight π character of the C8−C9 single bond due to the π delocalization of the charge that is transferring to **3**, which is delocalized on the C8 carboxylic group. These features that are present also in **IN** and **TS2** allow an effective stabilization of the positive and negative charges that are developing along the nucleophilic attack of the furan ring to the conjugated position of **3** and make **8** and **3** behave as a Michael donor and acceptor, respectively, rather than a diene and dienophile.

For **IN** the value of the C5−C7 BO (0.69) indicates that the C5−C7 single bond is practically formed, while the C2−C8 BO (0.12) presents a value similar to that in **TS1**. For **TS2** the

BO value of the C2−C8 forming bond (0.17) is in agreement with the early character of this TS along the closure of the zwitterionic intermediate **IN**.

Finally, the natural bond orbital analysis allows us to evaluate the charge transferred along the cycloaddition process.[10] The atomic charges have been shared between the donor 2-methylfuran **8** and the acceptor acetylenedicarboxylic acid **3**. The values of the charge transferred in **TS1**, **IN**, and **TS2** are 0.38, 0.44, and 0.41 au, respectively. These values indicate an increase of the charge transferred along the nucleophilic attack of the furan ring of **8** to the conjugated acetylenic system of **3** up to formation of the zwitterionic intermediate **IN**. The charge transferred at this intermediate is lower than that for the cycloaddition reaction between 1-methylpyrrole **5** and the diester **2** (0.71 au),[10] because the character of the oxygen atom of the furan ring is more electronegative than that of the nitrogen atom of the pyrrole ring.

The values of the dipole moments for **TS1**, **IN**, and **TS2** are 3.62, 4.17, and 3.74 D, respectively. These low dipole moments contrast with the large charge transfer along the cycloaddition process[8a] and can be due to an effective charge delocalization along the furan ring and the carboxylate groups in these species. A similar result has been found for the reaction between **5** and **2**, for which the inclusion of the solvent effect does not modify substantially the stepwise nature of the mechanism.[10]

Conclusions

The following conclusions can be drawn from the results reported in this DFT study: (i) The cycloaddition reaction of 2-methylfuran with acetylenedicarboxylic acid takes place along a stepwise mechanism. The process is initialized by the nucleophilic attack of the C5 position of the furan ring to one conjugated position of the acetylene system to give a zwitterionic intermediate, which by a subsequent ring closure affords the final cycloadduct. (ii) The PES around TSs and the intermediate is very flat, and DFT calculations carried out at the B3LYP/6-31G* level afford only the TS corresponding to the closure step. However, the inclusion of diffuse functions at the 6-31+G* level allow the localization and characterization of the corresponding stationary points, which are in a narrow range of 0.2 kcal/mol. (iii) Because **TS1**, **IN**, and **TS2** are energetic and structurally related, the cycloaddition process can be considered as a nucleophilic attack of **8** to **3** with concomitant ring closure. (iv) The low BO value between the C2 and C8 atoms at **TS1** together with the low participation of the component associated with C2−C8 length in the corresponding transition vector must be

attributed to stabilizing electronic factors instead of a bond forming process. Similar results have been found in related [4+2] cycloadditions where only one very asynchronous TS has been found and for which the analysis of geometrical data, BO_s, and the transition vector give results closer to **TS1**. These cycloadditions correspond to a non concerted process where one σ bond is being formed previously to the formation of the other one.

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