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A DFT Study of the Pericyclic/Pseudopericyclic Character of Cycloaddition Reactions of Ethylene and Formaldehyde to Buta-1,3-dien-1-one and Derivatives

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Cycloaddition reactions of ethylene and formaldehyde to buta-1,3-dien-1-one and derivatives were studied by performing a density functional theory study with the 6-31+G* basis set. Reactants, products, and transition states for each reaction were localized, and the path connecting reactants and products was also obtained. Magnetic properties were evaluated along the reaction path to elucidate the characteristics of the reactions studied. Also, a natural bond orbital analysis was performed to study the orbital interactions in the transition states. Calculations indicate that all reactions are pericyclic except three cases, which are pseudopericyclic reactions. In the latter, transition states are almost planar, and magnetic properties do not reveal aromatization enhancement in their transition states. Also, though the participation of lone pairs diminish the pericyclic character of the reactions, sometimes this participation is not enough to generate a change to a pseudopericyclic path. Overall, magnetic properties reveal as a good criterion to elucidate the characteristics of the reactions studied, though a combined application of several criteria is recommended.

1. Introduction

In 1976, Lemal and co-workers found that the reaction of automerization of a sulfoxide by means of a sigmatropic displacement proceeded easily.[1] The authors argued that the process was not typically pericyclic, as it presented different characteristics. As a consequence, the term *pseudopericyclic reaction* was proposed to denote such reactions, characterized by a concerted transformation whose primary changes in bonding encompass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbitals interchange roles. The role interchanging implies a disconnection in the cyclic array of overlapping orbitals because the atomic orbital switching functions are mutually orthogonal. Hence, pseudopericyclic reactions cannot be orbital symmetry forbidden.

Following Lemal's work, pseudopericyclic reactions did not attract much attention until Birney first,[2−10] and several other authors[11−19] revived interest in them by showing that a number of organic syntheses involve this type of process. As a result of Birney's works, a series of characteristics have been attributed to pseudopericyclic reactions: planar transition states, low activation energies, disconnections in orbital overlap, and impossibility of being symmetry forbidden.

Though Lemal's definition seems clear, the orbital description is not unique as the transformation between bonding and nonbonding orbitals is not univocally defined. In fact, no definitive criterion exists which allows a pseudopericyclic reaction to be distinguished from a normal pericyclic reaction and some controversy has arisen about how several reactions must be classified.[20−23]

In this context, the study of magnetic properties and their relation with aromaticity has appeared as one of the most useful criteria to distinguish between both types of mechanism. It is known that aromatization affects magnetic properties such as magnetic susceptibility and its anisotropy,[23−25] leading to especially negative values for such properties. Pericyclic reactions exhibit an enhancement of the aromaticity near the transition states, whereas pseudopericyclic reactions do not[23−28] Therefore, magnetic properties in the transition state should behave differently for both mechanisms. Herges et al. showed that,[24] for Diels−Alder reaction, an important decrease in these magnitudes occurs in the transition state respect to reactants or products. On the other hand, the typical disconnection of pseudopericyclic reactions would have prevented this aromatization, as shown by our group in previous work,[21,23,29−32] allowing both types of reactions to be distinguished.

The previously mentioned quantities are global properties, which can be affected by parts of the molecule not directly implicated in the aromatization process. To avoid this problem, a useful property is the Nucleus Independent Chemical Shift (NICS) proposed by Schleyer et al. and defined as the negative of the magnetic shielding.[33] This property can be evaluated at any point of the molecule, and exhibits negative values in the center of aromatic rings.

Another method that uses magnetic properties is ACID (Anisotropy of the current-induced density), recently developed by Herges and Geuenich.[34] This method was successfully applied in our research group in recent work,[30−32] and it has revealed as a very useful tool for the study of delocalization in molecules. The method allows the visualization of the ring

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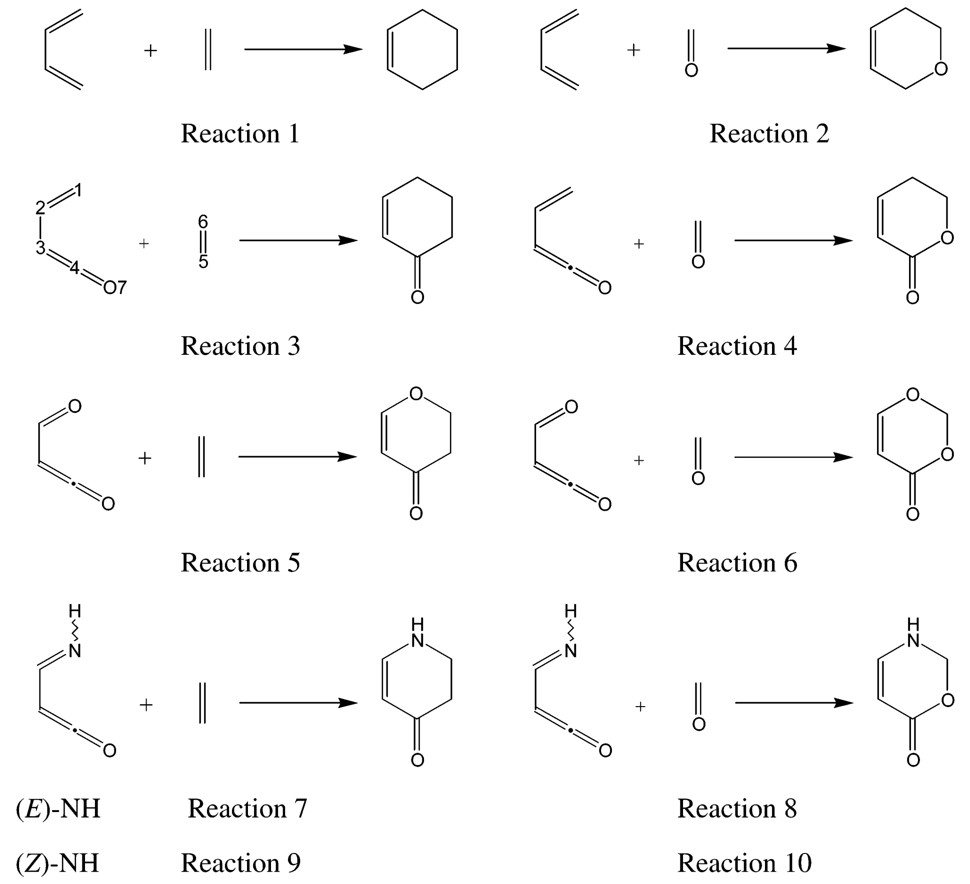

Figure 1. Reactions studied and numbering scheme.

current formed when a magnetic field is applied and permits to decide whether there is a disconnection on the cyclic array of orbitals.[30,31,35,36]

Despite the variety of methods, a systematic application is necessary to confirm the validity and performance for different types of reactions. In our research group, several studies have been performed applying some of these criteria to groups of reactions, allowing the characterization of the reactions as pericyclic or pseudopericyclic.[21,23,29−32] Most of the previous studies deal with electrocyclization reactions, so in the present paper we extend the study to cycloaddition reactions.

Therefore, we conducted a comprehensive density functional theory (DFT) study of the cycloaddition reactions presented in Figure 1. These are cycloaddition reactions of ethylene and formaldehyde to buta-1,3-dien-1-one and substituted derivatives. Also, additions of ethylene and formaldehyde to 1,3-butadiene have been studied as a reference for the observed behaviors. Most of these reactions are experimentally known as substituted systems.[37−42] Birney et al. have previously studied from a theoretical point of view reactions 4 and 6 with formaldimine instead of formaldehyde as dienophile.[8] Also, there exists a previous study in which the energetical and geometrical characteristics on reaction 5 have been analyzed in terms of MP2/6-31G* calculations.[43]

This group of reactions exhibits a variety of potential orbital disconnections to be present, suggesting the possibility of a pseudopericyclic mechanism. It should be remembered here that one disconnection is enough for a reaction to be pseudopericyclic.[4,30] Normally, such disconnections are associated to interactions of the lone pairs though, as shown in previous work, the possibility of interaction with lone pairs does not necessarily imply pseudopericyclic character.[23,44]

TABLE 1: Calculated Energies in kcal/mol, Including Zero-Point Energy Corrections for the Species Participating in the Reactions Studied Relative to the Reactants in *s*-trans Conformation

	s-cis	TS	prod		*s*-cis	TS	prod
1	3.51	27.06	-32.42	2	3.51	26.32	-17.52
3	1.67	25.29	-41.83	4	1.67	17.48	-39.35
5	0.37	23.06	-23.67	6	0.37	6.21	-19.21
7	0.48	24.01	-38.43	8	0.48	5.78	-35.21
9	1.91	29.14	-39.39	10	1.91	21.82	-36.17

2. Computational Details

The geometry of each stationary point corresponding to reactants, products, and transition states was fully optimized using the Gaussian98 software package[45] with the 6-31+G* basis set and the density functional theory (specifically, the Becke3LYP functional).[46,47] All points were characterized as minima or transition structures by calculating the harmonic vibrational frequencies, using analytical second derivatives. Also, the pathway for each reaction was obtained by using the intrinsic reaction coordinate (IRC) with mass-weighted coordinates. Although the evaluation of the absolute aromaticity of a compound remains a controversial issue,[48] we were primarily interested in its variation during the reaction, and the evaluation of magnetic properties can be a useful tool for this purpose. Changes in magnetic properties along the IRC were monitored at different points along the IRC for which the mean magnetic susceptibility (χ), its anisotropy (χ_{anis}), and NICS were calculated. Magnetic susceptibility values were calculated by computing the NMR shielding tensors using the IGAIM (individual gauges for atoms in molecules) method,[49,50] which is a slight variation of the CSGT (continuous set of gauge transformations) method.[51] NICS was calculated with the GIAO (gauge-

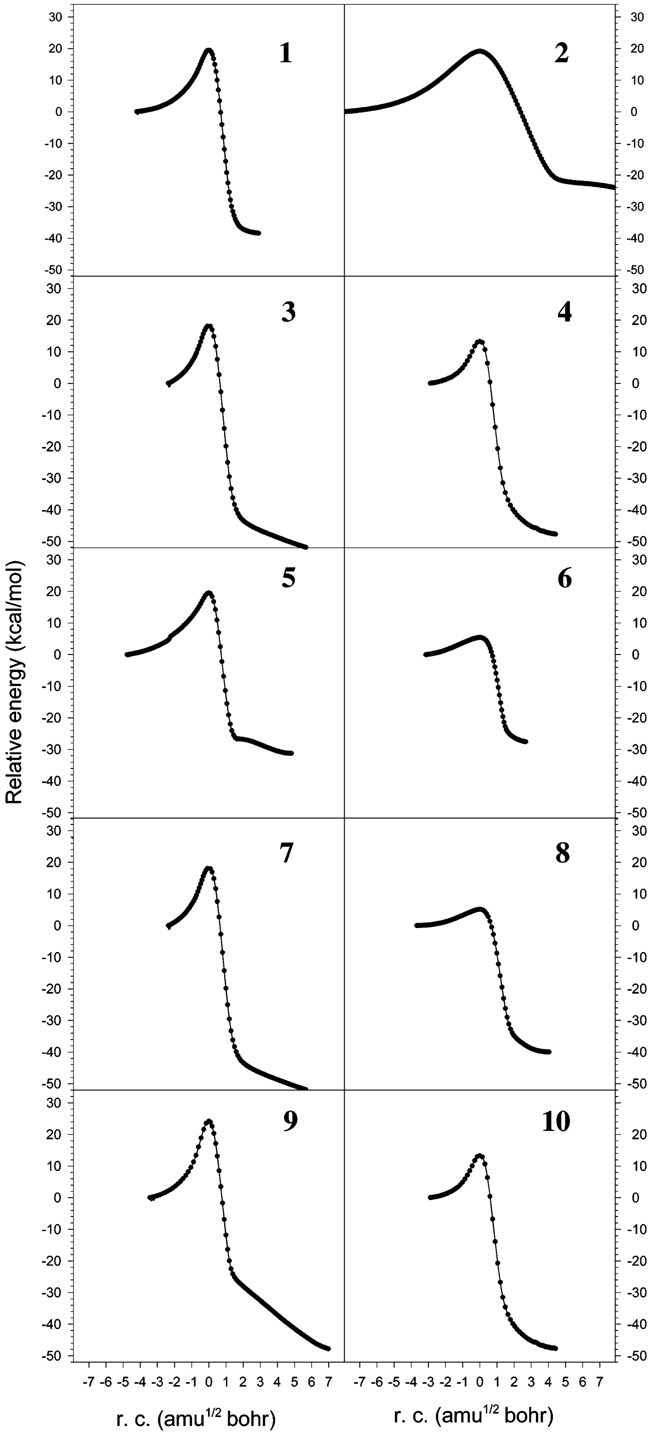

Figure 2. Variation of energy along the reaction path relative to reactants in *s-cis* conformation.

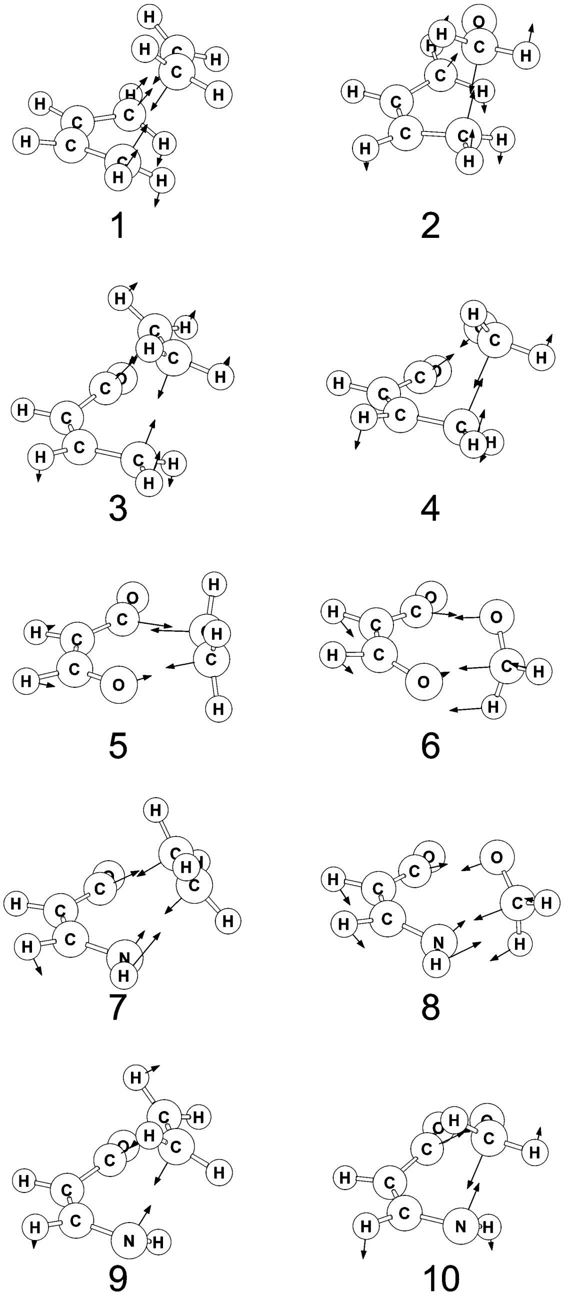

Figure 3. Transition structures and normal mode eigenvectors for the coordinate frequency of the reactions studied.

independent atomic orbital) method.[52] We have also carried out some ACID calculations (anisotropy of the current-induced density) with the program supplied by Herges.[34] Furthermore, a natural bond orbital (NBO) analysis was performed in the transition state of each reaction in order to get insight about the relevant interactions leading to the formation of the new bonds.[53−55]

3. Results

3.1. Energies and Geometries. Table 1 shows the energies for the different species participating in the reactions studied, relative to reactants in the most stable conformation (*s*-trans), and corrected for zero point energy (ZPE). It should be noted here that only the *s*-cis conformation is susceptible of [4+2] addition, so a conformational change is the first step for all these reactions. Though the need to calculate full IRC'S prevented us from using a larger basis set or a sophisticated post-HF method, the activation energy and reaction enthalpy obtained for reaction 1 agree reasonably well with values from literature.[24,56,57]

All reactions with ethylene as dienophile present moderate energy barriers, which vary between 23 and 29 kcal/mol, and all of them are exothermic. Comparing these values in Table 1, it seems that the presence of the ketene group or the lone pairs in nitrogen or oxygen hardly affects the barrier height. Therefore, as barriers are concerned no significant differences are observed respect to the prototypical pericyclic reaction 1.

In the group of reactions with formaldehyde as dienophile, differences are larger. Reaction 2 presents a barrier similar to

TABLE 2: Selected Geometrical Parameters for the Transition States of the Reactions Studied[a]

	TS1	TS3	TS5	TS7	TS9	TS2	TS4	TS6	TS8	TS10
R_{1-6}	2.267	2.338	2.209	2.230	2.270	1.976	2.059	2.192	2.165	2.003
R_{4-5}	2.265	2.182	2.108	2.169	2.053	2.170	2.138	2.153	2.262	1.980
θ_{216}	102.2	97.7	116.0	110.4	97.9	101.1	98.2	111.8	114.5	96.6
θ_{345}	102.2	105.9	114.6	110.2	109.3	100.8	99.2	100.2	98.9	104.7
φ_{1234}	0.0	16.7	0.0	13.9	−23.4	−2.6	−8.5	−7.3	−7.8	−18.3
φ_{2345}	57.9	44.6	0.0	30.2	−35.9	51.1	−41.9	−17.9	−26.3	−24.4
φ_{3456}	−49.5	−41.5	0.0	−34.3	33.4	−35.6	31.6	57.9	62.7	4.1
φ_{4561}	0.0	−2.1	0.0	6.2	5.9	−16.4	14.3	−54.1	−49.4	35.7
φ_{5612}	49.5	49.0	0.0	30.2	−49.4	62.5	−57.3	29.7	17.4	−66.2
φ_{6123}	−57.9	−63.5	0.0	−45.8	64.0	−58.6	62.2	8.5	21.8	61.7
φ_{7432}	−	−140.1	0.0	−158.1	153.3	−	146.3	170.3	163.5	161.6
φ_{7456}	−	141.1	0.0	150.4	−152.3	−	−151.6	−125.4	−120.7	−178.9

[a] Distances in Å, angles in deg. See Figure 1 for numbering.

TABLE 3: Selected Second Order Perturbation Theory Interactions[a]

donor	acceptor	TS1	TS3	TS5	TS7	TS9	TS2	TS4	TS6	TS8	TS10
π_{12}	π^*_{56}	15.89	15.25		7.50	14.74	66.19	52.67			43.79
π_{34}	π^*_{56}	15.82	15.79		7.56	18.65					
LP(1)	π^*_{56}	#	#	22.07	16.44		#	#	23.56	34.84	7.18
π_{56}	π^*_{12}	10.77	5.18				8.94				
π_{56}	π^*_{34}	10.72	16.64		13.86	28.54	8.15	5.67			6.55
π_{56}	π^*_{47}	#	7.35	48.51	19.63	16.51	#	5.04			11.94
LP(5)	π^*_{34}	#	#	#	#	#	6.90	6.81			13.09
LP(5)	π^*_{47}	#	#	#	#	#	#		23.86	11.82	7.73

[a] A # indicates a nonexistent interaction, whereas empty cells indicate an interaction smaller than 5 kcal/mol. See Figure 1 for numbering.

TABLE 4: Selected NLMO Bond Order Contributions to the Forming Bonds[a]

		TS1	TS3	TS5	TS7	TS9	TS2	TS4	TS6	TS8	TS10
1-6	$\pi_{\mathbf{12}}$	0.066	0.122		0.050	0.117	0.226	0.225			0.194
	$\pi_{\mathbf{34}}$	0.064	0.050			0.046	0.050	0.054			0.033
	LP(1)	#	#	0.108	0.069		#	#	0.087	0.124	
	$\pi_{\mathbf{56}}$	0.101	0.034				0.056				
4-5	π_{12}	0.064	0.037				0.052	0.030			
	π_{34}	0.066	0.056			0.053	0.029				
	π_{56}	0.101	0.141	0.231	0.196	0.213	0.074	0.057			0.078
	LP(5)	#	#	#	#	#			0.079	0.049	0.032

[a] A # indicates a nonexistent interaction, whereas empty cells indicate a contribution smaller than 0.025. See Figure 1 for numbering.

those obtained with ethylene, though somewhat smaller probably due to the participation of oxygen lone pairs in the formation of the new C−O bond. Though barriers are smaller for reactions 4 and 10, the values are still significant. Finally, reactions 6 and 8 present much smaller barriers, due to the possibility of lone pairs to participate in the formation of the two new bonds. It should be indicated that, contrary to reactions with ethylene, the configuration of the imine group affects significantly the energy barrier, suggesting a different mechanism for *Z* than for *E* configuration. The above-described behavior is easily observed in Figure 2, which shows the energy changes along the reaction path relative to reactants. All reactions exhibit similar profiles except reactions 6 and 8, which present smaller barriers. Pseudopericyclic reactions usually exhibit small activation energies so reactions 6 and 8 are candidates for a pseudopericyclic mechanism.

According to Birney et al., pseudopericyclic reactions have planar or almost planar transition states.[4] Table 2 shows selected geometric parameters for the transition states of the reactions studied, which are displayed in Figure 3 together with the transition vectors corresponding to the cycloaddition reactions. Most relevant parameters are the distances of the forming bonds and the planarity of the six atoms that form the ring. All distances have values around 2.0−2.3 Å, typical of this kind or reaction. As regards planarity, for the prototype pericyclic reaction 1, the deviation is significant, as revealed by dihedrals $\varphi_{6-1-2-3}$ and $\varphi_{2-3-4-5}$. Such a nonplanar transition state is characteristic of pericyclic reactions, which must deform the structure to obtain a convenient orbital overlap. The analogous reaction 2 shows a similar structure with a marked deviation from planarity. The presence of the ketene group in reactions 3 and 4 increases the planarity around atom 4, but structures are still clearly nonplanar. A further increase of the planarity is observed when nitrogen is present in the diene, especially for reaction 8. The most striking cases correspond to reactions 5 and 6. Transition state for reaction 5 is totally planar indicating pseudopericyclic character, because it is not possible to construct a cyclic loop with the interacting π orbitals. Transition state for reaction 5 was found to be nonplanar at MP2/6-31G* level.[43] However, calculations performed at QCISD/ 6-311+G(2d,p) give a transition structure in which deviations from planarity are half than those obtained with MP2/6-31G*, showing values similar to those found for reaction 8.

Reaction 6 is almost planar and only marginal deviations are observed because the oxygen atom is placed slightly out of the plane. Therefore, as regarding geometries, only 5, 6, and probably 8 can be pseudopericyclic reactions. However, as shown in Table 1, reaction 5 shows a quite large barrier though for pseudopericyclic reactions small barriers are expected.[4] In fact, pseudopericyclic reactions present smaller barriers relative to pericyclic alternatives, so absolute values do not always reflect the mechanism of the reaction. As a consequence, pseudoperi-

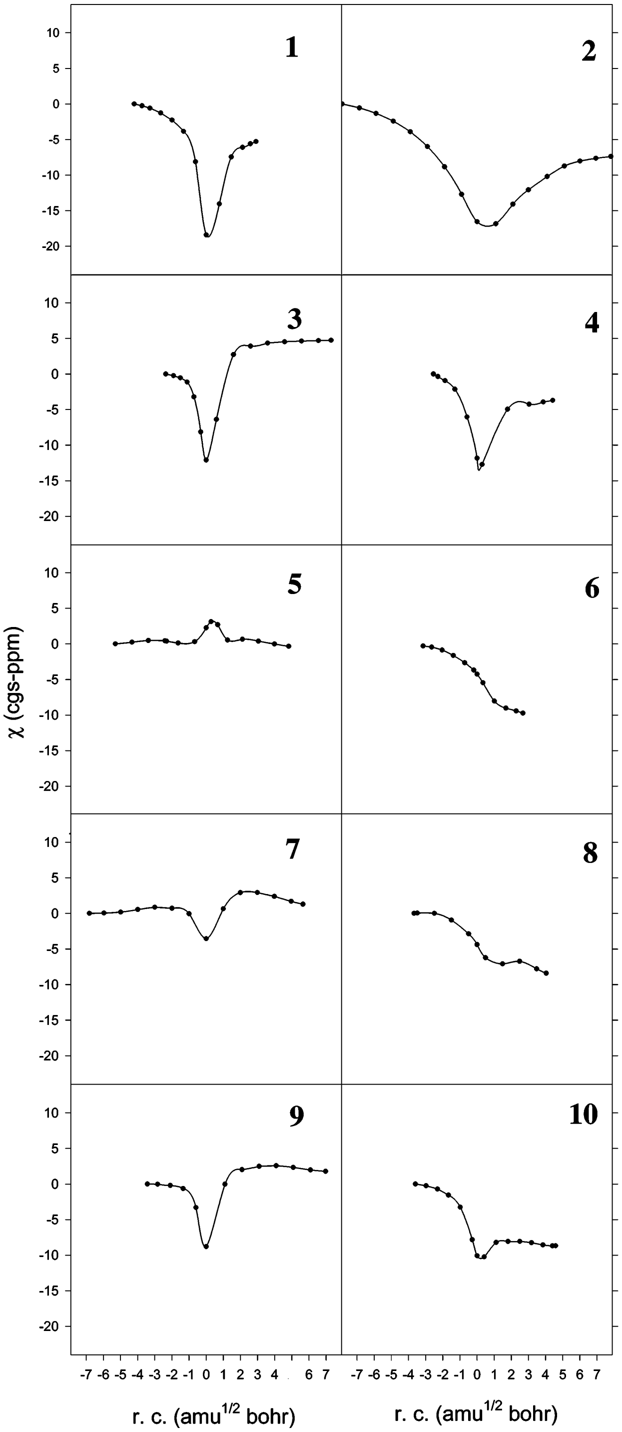

Figure 4. Variation of mean magnetic susceptibility along the reaction path relative to reactants.

cyclic reactions can exhibit quite large barriers as happens in pseudopericyclic Boulton-Katritzky rearrangement of(5*R*)-4-nitrosobenz[*c*]isoxazole and its anion.[31]

3.2. NBO Analysis. More information about the processes studied can be obtained by means of a NBO analysis of the transition states.[53-55] The results thus obtained were analyzed in terms of the second-order perturbation theory and NLMO (natural localized molecular orbitals), as shown in Tables 3 and 4.

Second-order perturbation theory in NBO gives the energy lowering obtained when electrons from partially occupied orbitals are allowed to delocalize into partially empty orbitals. A large energy implies a huge tendency to delocalization and therefore, it can be used as an indicator of electron movements. Only selected intermolecular interactions are listed in Table 3, as they are the only of interest for the processes studied. For reaction 1, the main interactions are of similar magnitude, corresponding to the three double bonds of the system, as expected for a pericyclic reaction. A similar behavior is observed for reaction 3, where the presence of the ketene group does not introduce any significant change; that is, the main orbital interactions take place among the π orbitals located on the three C═C bonds, though in this case there is a participation of the exocyclic C═O bond. The corresponding reactions with formaldehyde (2, 4) show a somewhat more complicated pattern. Thus, for these reactions the interactions are not symmetric, and a large interaction between π_{12} and π^*_{56} orbitals dominates.

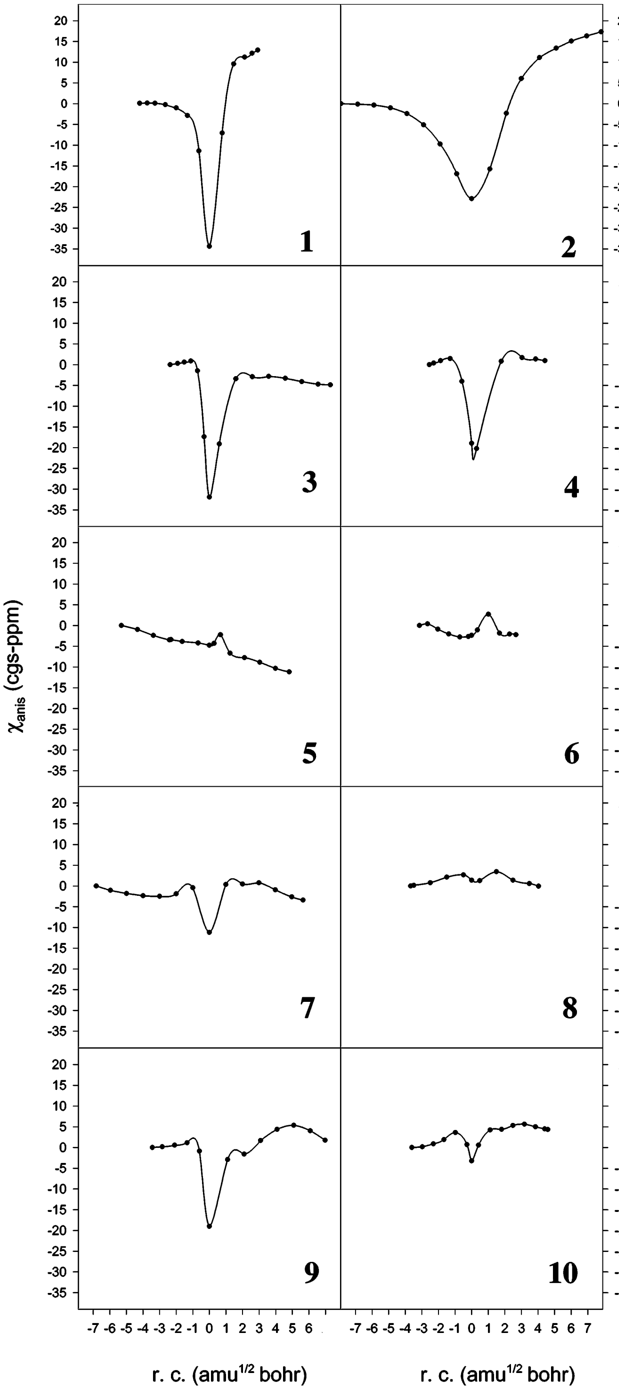

Figure 5. Variation of the anisotropy of the magnetic susceptibility along the reaction path relative to reactants.

All other energies are smaller, but reflect the interactions between C═C and C═O bonds, as for a pericyclic reaction, despite the participation of lone pairs. As noted before, the participation of a lone pair does not imply pseudopericyclic character, though it "pushes" the reaction to a pseudopericyclic mechanism.[21,44]

For reaction 5, a different pattern is observed. In this case, the interaction is dominated by the lone pair delocalization into ethylene double bond, and the interaction of C═C of ethylene into the ketene exo C═O bond. That is, all relevant interactions take place between orbitals located in the molecular plane, indicating that nor cyclic loop of interacting π orbitals is formed, nor aromaticity can be present. Therefore, this reaction should be classified as pseudopericyclic. Reaction 6 shows a similar behavior, but in this case, the presence of lone pairs on formaldehyde gives an interaction totally dominated by the lone pairs. Interactions involving π orbitals from the diene are insignificant.

Let us analyze reactions 7, 8, 9, and 10, those with a NH group. For reactions 9 and 10, there are no doubts, as the configuration of the imine prevents the lone pair of the nitrogen to participate directly in the formation of the new bonds. Therefore, the behavior is similar to that observed for reactions 3 and 4. For reaction 7, however, the new C−N bond is formed with contributions from nitrogen lone pair and C═N double bond, the former being twice the latter. In reaction 8 the lone pair interactions dominate indicating pseudopericyclic character.

NBO gives other sources of useful information as that obtained from NLMO analysis. Table 4 lists the bond order contributions from NLMO to the new bonds formed. In reaction 1, the new bonds are formed mainly from contributions of the three C═C bonds, with more participation of those from the diene. In reactions 2, 3, 4, 9, and 10, the behavior is similar and the main contributions to the new bonds come from π orbitals. In pseudopericyclic reactions 5, 6, and 8, the behavior is totally different, the new bonds being dominated from contributions from the LP's or from C═C in-plane bond (reaction 5). Finally, the most ambiguous case is reaction 7, where the new C−N bond comes from contributions from nitrogen lone pair and C═N bond of similar magnitudes. In summary, as obtained from NBO analysis, reactions 5, 6 and 8 are clearly pseudopericyclic, whereas reaction 7 shows a mixed behavior.

3.3. Magnetic Susceptibility. Figure 4 shows the variation of the mean magnetic susceptibility along the reaction path. As noted by other authors, the presence of aromaticity is accompanied by quite negative values of the magnetic susceptibility.[23,24,29,30] Therefore, in a pericyclic reaction, with an enhanced aromaticity in the transition state, a minimum in the magnetic susceptibility should be observed relative to other points of the reaction path. As shown in Figure 4, the cycloaddition reactions of ethylene show in most cases a clear minimum near the transition state, indicating aromaticity enhancement and pericyclic character. The only exception to this behavior is reaction 5, which shows a small maximum instead of a minimum, corresponding to a pseudopericyclic reaction. Also, it can be observed that the inclusion of NH group in *E* configuration diminish the pericyclic character of the reactions, especially for reaction 7, where, due to the participation of the lone pair, the relative aromaticity in the transition state is not so large, as corresponds to a borderline case. However, the differences on magnetic properties between the TS's of these reactions should also be partially adscribed to the low intensity of ring currents in nitrogen compounds.[58] As regards to reactions with formaldehyde, two reactions do not present a minimum in the transition state and are classified as pseudopericyclic (6 and 8).

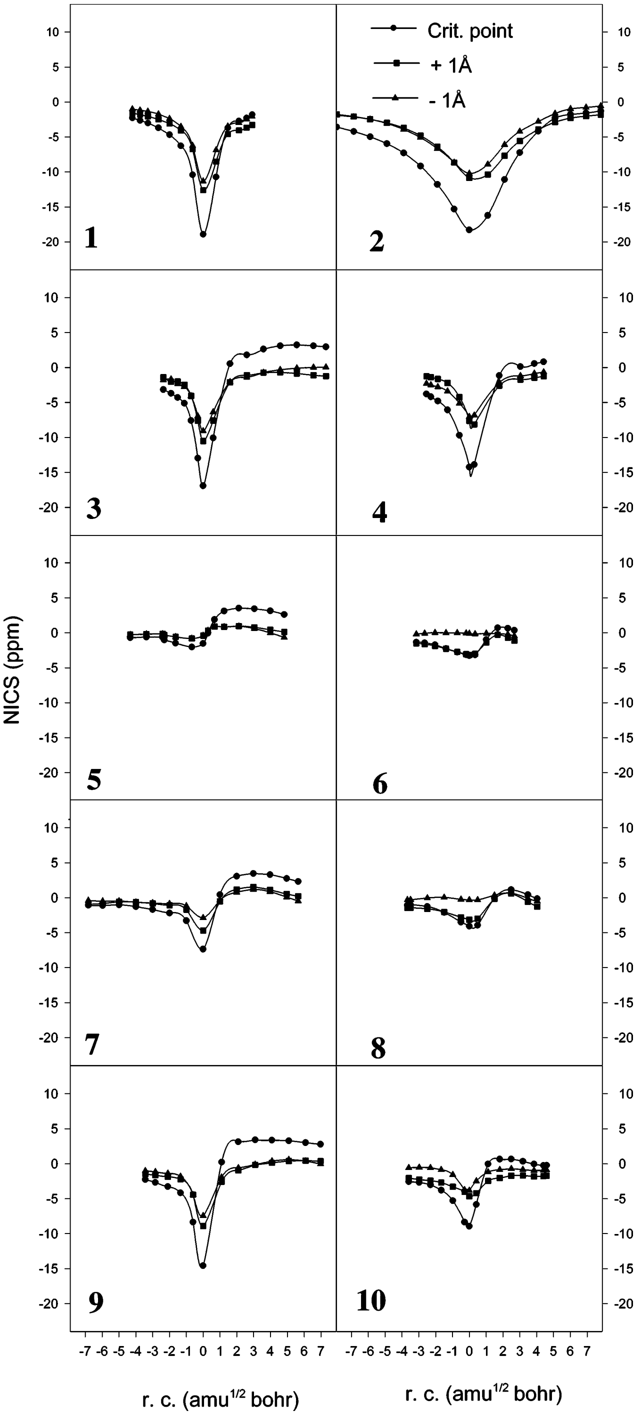

Figure 6. Variation of NICS along the reaction path.

Anisotropy of the magnetic susceptibility can also be employed as criteria of aromaticity in a way similar to the previous case. A minimum in the transition state indicates development of aromaticity and pericyclic character. As can be seen from Figure 5, all reactions exhibit a minimum near r.c. = 0 except reactions 5, 6, and 8, indicating pseudopericyclic character for these reactions in agreement with previous considerations.

3.4. NICS. Contrary to magnetic susceptibility, the NICS index defined by Schleyer as the negative of the magnetic shielding,[33] can be evaluated at a point, avoiding some of the problems associated to global properties as χ. In his works,[33,59]

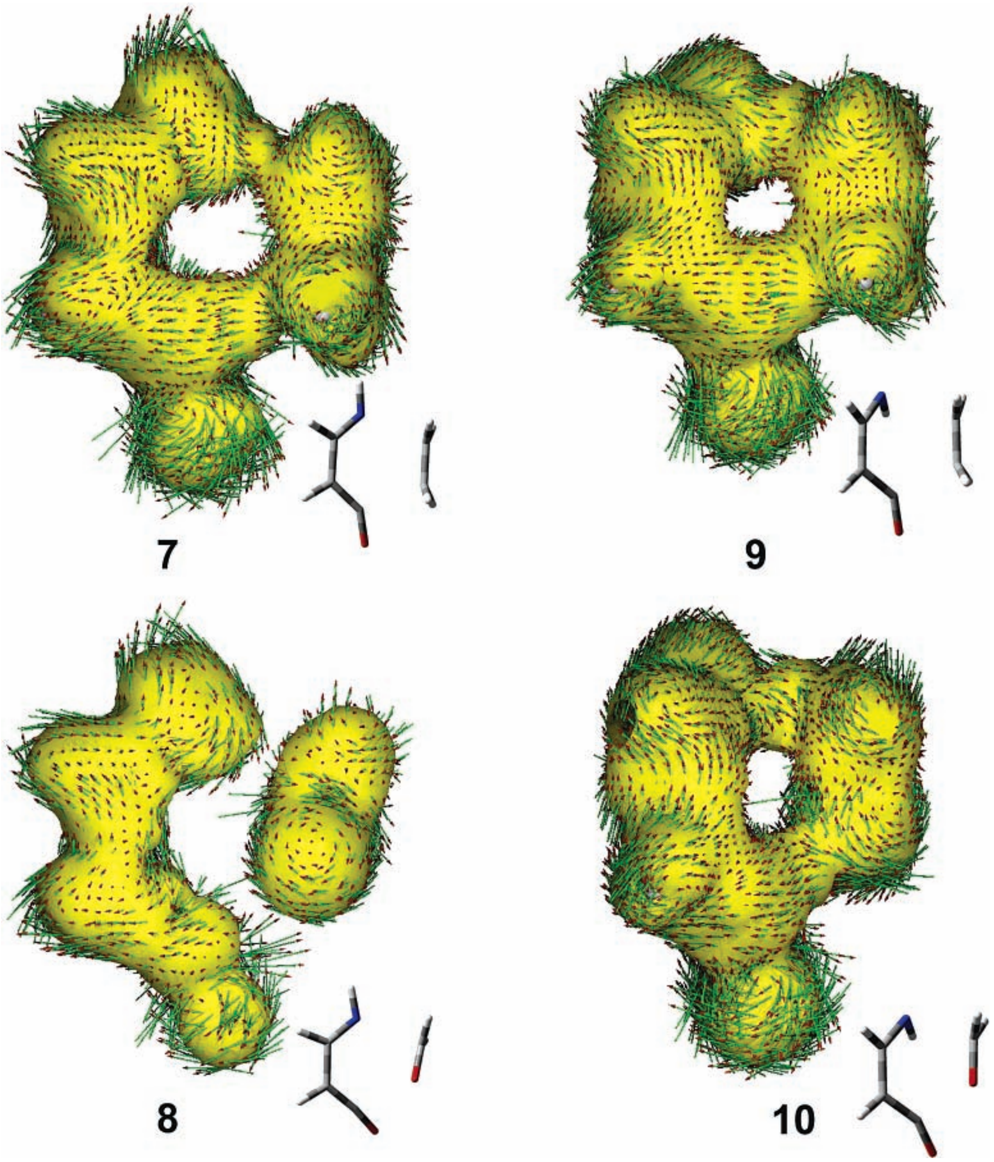

Figure 7. ACID plots in the transition state for selected reactions. Isosurface value is 0.02, and magnetic field points from the paper to the reader.

Schleyer chose to evaluate NICS at the geometrical center of the ring or at the ring critical point as obtained from Bader's atoms-in-molecules theory.[60,61] Moreover, he prevented to obtain NICS in the molecular plane due to the contributions of the σ bonds to the shielding, and suggested to calculate it out of the plane, more precisely at 1 Å above the plane of the aromatic molecule.[62] In the present case, we are dealing with transition states which are nonplanar, so it is different to calculate NICS above or below the ring. As a consequence, we opted to calculate NICS at three different points: the ring critical point and 1 Å above and below the ring critical plane. The results are shown in Figure 6.

The variation of NICS along the reaction path clearly shows minima near the transition states for reactions 1−4 for the three points considered. These minima indicate a larger shielding in the transition state and therefore aromaticity enhancement. Even for reactions 7, 9, and 10, the pattern is similar though the minima are much less deeper in comparison with those of the previous reactions. Reactions 5, 6, and 8 exhibit a different profile with no minimum or a very shallow one. The presence of these shallow minima difficults the assignment of the character of the reactions based on NICS, though we believe that the observed behavior allows these reactions to be classified as pseudopericyclic.

3.5. ACID. Another property which allows determining whether a system is aromatic is the anisotropy of the current-induced density (ACID).[34] When a magnetic field is applied to an aromatic molecule, an induced current density is generated. In an aromatic system, the current describes a loop in a diatropic way, whereas for an antiaromatic system, the induced current is paratropic. Moreover, in a nonaromatic system no cyclic current is observed. With ACID method the anisotropy of the current-induced density can be analyzed, and critical isosurface values can be obtained (CIV) which allow us to measure the degree of delocalization (CIV is the isosurface value at which the topology changes from a cyclic to an open one).

A group of reactions exhibits quite large CIV's (0.068, 0.069, 0.060, 0.052, for reactions 1, 2, 3, and 4, respectively) indicating a large delocalization and thus aromatic character for those transition states. Also, a quite large value of 0.047 is obtained for reaction 9, and a moderate value of 0.038 for reaction 10. Therefore, the presence of NH group in reactions 9 and 10 diminish the values for CIV, but they are still large enough showing that no disconnection occurs in the transition state and therefore aromaticity is present. The situation is completely different in transition states of reactions 5, 6, and 8. Here, small CIV's, less than 0.015 are obtained, indicating a disconnection in the topology of the induced current and therefore a lack of aromaticity. Reaction 7 shows a CIV of 0.028, which indicates that there is probably no disconnection, but that this reaction is a borderline between pericyclic and pseudopericyclic character.

The values of CIV give us information about the induced current, but not about the aromaticity of the structure (a highly antiaromatic system also shows high CIV). A picture of the current density vectors can be plotted onto an isosurface of anisotropy of the induced current density, allowing a diagnosis about the aromaticity of the system. Such pictures are shown in Figure 7 for selected reactions. As can be seen, for reactions 9 and 10 a diatropic current is clearly observed indicating the pericyclic nature of these reactions, as also happens in reaction 7, though more weakly. Finally, reaction 8 shows a clear disconnection indicating the nonaromatic character of the structure.

4. Conclusions

Cycloaddition reactions of ethylene and formaldehyde to buta-1,3-dien-1-one and derivatives were studied by performing a DFT study with the 6-31+G* basis set. Magnetic properties were evaluated along the reaction path to elucidate the characteristics of the reactions studied. Also, a NBO analysis was performed to study the orbital interactions in the transition states.

As regards reactions with ethylene, all criteria employed in this work indicate that reactions 1, 3, and 9 are clearly pericyclic, with large activation energies, nonplanar geometries in the transition states, and also a significant aromatization enhancement in the transition state as revealed by magnetic properties. Reaction 5 presents a significant energy barrier, but all criteria indicate this reaction to be pseudopericyclic. Reaction 7 is a borderline case; NBO analysis indicates a substantial participation of the lone pair on nitrogen in the formation of the new bond, as revealed by NLMO and second-order perturbation theory. However, magnetic properties indicate that this reaction preserve characteristic properties of pericyclic reactions, as confirmed by the presence of a ring current revealed by ACID. Reactions with formaldehyde showed similar behavior; thus, reactions 2, 4, and 10 are clearly pericyclic with all criteria thus employed, whereas reaction 6 and reaction 8 are clearly pseudopericyclic.

In conclusion, the presence of the ketene group together with lone pairs on nitrogen and formaldehyde is able to promote a change to a pseudopericyclic mechanism, as shown for reactions 6 and 8. However, when the reactions occur with ethylene, only a pseudopericyclic reaction is obtained when lone pairs on oxygen atoms participate (reaction 5), but not when the lone pair belongs to a nitrogen atom as in reaction 7.

Overall, magnetic criteria seemed to be effective to elucidate the mechanism of the reactions studied. However, some problems arise with intermediate cases, due to small aromatization enhancement in the transition states, leading to not so well defined behaviors. Therefore, a combined application of several criteria is recommended.

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Supporting Information Available: Listings of geometries and ACID plots for transition states. Energies for all species participating in the reactions. This material is available free of charge via the Internet at http://pubs.acs.org. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

References and Notes

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