Diels−Alder Reactions of 2-Azabutadienes with Aldehydes: Ab Initio and Density Functional Theoretical Study of the Reaction Mechanism, Regioselectivity, Acid Catalysis, and Stereoselectivity†

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The Diels−Alder reaction of 2-azabutadiene with aldehydes has been studied using high level ab initio molecular orbital and density functional methods. Multiconfigurational calculations were carried out on the concerted and stepwise mechanisms. At the CASPT2F/6-31G*//CASSCF/6-31G* level of theory, the [π4s + π2s]-cycloaddition of 2-azabutadiene with formaldehyde is predicted to be a concerted reaction, in good agreement with the experimental evidence. The regio- and stereoselectivity of the reaction was studied at the HF/6-31G*, MP2/6-31G*, and Becke3LYP/6-31G* levels of theory. The density functional calculations appears to give a good description of the basic features of the reaction. The decisive role played by the Lewis acid catalyst in reducing the reaction barrier and increasing the stereoselectivity was evaluated. It is shown that the Lewis acid coordination to the dienophile significantly changes the geometrical and electronic character of the transition structure. The electrostatic interaction between the Lewis acid and the nitrogen lone pair of the 2-azabutadiene appears to be important in the preference for the *exo*-coordination of the catalyst in the transition structure.

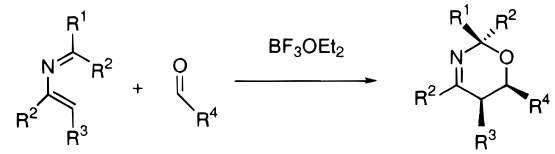
Introduction

The increasingly growing number of heterodienes and heterodienophiles is making the hetero Diels−Alder reaction a very attractive tool in organic synthesis, especially in the areas of heterocycles and natural products synthesis.[1]

Due to the great diversity of heterodienes and heterodienophiles, many different types of hetero Diels−Alder reactions are possible. However, the most widely used heterodienes are probably the nitrogen-containing dienes, mainly the 1-aza and 2-azabutadienes.[2,3] These type of systems have been shown to participate as 4π components in Diels−Alder cycloadditions with a variety of dienophiles.[1,2]

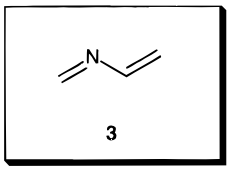
In this context, it has been found that the electronically neutral 2-azabutadienes **1** undergo a [4 + 2]-cycloaddition reaction with aldehydes to give, in a regio- and stereoselective manner, 1,3-oxazine derivatives **2** (see Scheme 1) with high yields.[4] The reaction usually requires the presence of catalytic amounts of boron trifluoride as Lewis acid catalyst, but in some instances, e.g., when using electron-deficient aldehydes, it takes place even without a Lewis acid catalyst. It can be concluded also, from the experimental evidence, that the reaction of 2-azabutadiene derivatives **1** with aldehydes takes place via a concerted [π4s + π2s] mechanism.[4]

Scheme 1



1 **2**

R^1, R^3 = alkyl; R^2 = aryl; R^4 = alkyl, aryl



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Since their discovery, the all-carbon Diels−Alder reactions have been intensively studied, and new theoretical methods were always applied to these reactions. After years of strong controversy, a concerted (while in many cases asynchronous) mechanism has finally emerged as the favored one.[5] On the other hand the hetero Diels−Alder reactions have been by far less studied from a theoretical point of view. However, there is an increase in the number of ab initio studies of several types of hetero Diels−Alder reactions,[6,7] which seems to parallel their growing interest as useful synthetic tools.

† The authors dedicate this paper to Prof. Dr. Juan Bertrán i Rusca on occasion of his 65th birthday.

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Thus, the Diels−Alder reaction of 2-azabutadienes with alkenes and alkynes has been studied previously using ab initio methods at the HF/3-21G* level of theory, and it was shown that the activation energies and asynchronicities of these reactions follow the same trends as the corresponding reactions of butadiene, the influence of the diene nitrogen being predicted to be small.[7]

In this paper, we theoretically address the mechanism of the Diels−Alder reactions of 2-azabutadienes **1** with aldehydes, by studying the competition between the concerted and the diradical stepwise mechanisms, the regio- and stereoselectivity of the reaction, and the influence of the Lewis acid catalysts on the reaction mechanism.

Computational Methods

The calculations reported here were carried out at the HF/6-31G*, MP2/6-31G*, Becke3LYP/6-31G*, MCSCF/6-31G*, and CASPT2F/6-31G*//MCSCF/6-31G* theory levels, using the GAUSSIAN 92,[8a] GAUSSIAN 94,[8b] and MOLCAS[9] programs. All the stationary points were fully optimized and characterized by vibrational frequency calculations. The charges were derived from the Mulliken population analysis. The geometries and energies of the stationary points located can be found in Supporting Information. The transition structures corresponding to the concerted reaction pathway are shown in Figure 1 (**TS1**-**TS4**), while those belonging to the stepwise mechanism can be found in Figure 2 (**TS5**, **TS6**). In addition the structures of the two diradical intermediates **DI1** and **DI2** located in the stepwise reaction pathway are shown in Figure 3.

The concerted and stepwise mechanisms for the thermal reaction of **3** with formaldehyde, to give the experimentally found 1,3-regioisomer, were studied with the MCSCF method using the GAUSSIAN 94 package. The active space used includes six electron in six orbitals: two π and π^* molecular orbitals of the 2-azabutadiene and the π and π^* of the formaldehyde. After the CASSCF optimization, CASPT2F/6-31G* single point calculations were carried out using the MOLCAS program. The CASPT2F single point calculations were carried out using a valence space of 10 orbitals and 10 electrons. In this case we add to the 6 electrons/6 orbitals space used for the geometry optimizations the two lone-pairs of the oxygen with a couple of corresponding virtual orbitals. This enlargment was necessary for having a better correlation of the lone-pairs of the oxygen. The CASPT2F method employs second-order perturbation theory to obtain the correlation energy for all the electrons in a system, starting from a MCSCF reference wave function. The CASPT2F method is the multiconfigurational equivalent of the MP2 method.

The concerted potential energy surfaces of the thermal and Lewis acid catalyzed Diels−Alder reaction of **3** with formaldehyde were studied at the HF/6-31G* and MP2/6-31G* levels of theory. In some cases, the activation energies were evaluated by single-point calculations at the MP2, MP3, and MP4 theory levels on the HF/6-31G* geometries. Also, the Lewis acid catalyzed reaction of **3** with acetaldehyde was studied at the HF/6-31G* level of theory (see Figure 5). In all cases the BH_3 was used as a model of the Lewis acid catalyst.

In addition to the ab initio molecular orbital calculations, we also carried out density functional calculations[10] on the concerted mechanism for the Diels−Alder reaction of **3** with formaldehyde at the Becke3LYP/6-31G* level which appears to adequately reproduce the activation energies of the several types of pericyclic reactions.[5b,11]

Results and Discussion

In the case of the all-carbon Diels−Alder reactions, calculations carried out at the HF/6-31G* and MP2/6-31G* levels of theory have been shown to gave good descriptions of the mechanism and substituent effects of the Diels−Alder reactions.[12] However, the monodeterminantal approach cannot give a balanced description of both the concerted and the stepwise diradical mechanisms. Thus, in the case of the prototypical Diels−Alder reaction of butadiene with ethylene, multiconfigurational (MCSCF) calculations have been carried out in order to properly characterize the potential energy surface of the concerted and stepwise mechanisms.[13]

There are no examples of MCSCF calculations of hetero Diels−Alder reactions but, as in the case of the all-carbon analogs, these reactions can, in principle, take place through concerted or stepwise mechanisms.

In order to determine the preferred reaction pathway for the [4 + 2]-cycloaddition of 2-azabutadienes with aldehydes, we carried out MCSCF calculations on the concerted and stepwise mechanisms for the model reaction of 2-azabutadiene **3** with formaldehyde to give the 1,3-adduct. The concert energy[14] for the reaction was then evaluated at the CASPT2F/6-31G*//CASSCF/6-31G* level of theory.

As the reaction of **3** with formaldehyde is predicted to take place via a concerted mechanism, the regioselectivity, acid catalysis, and stereoselectivity of the reaction were studied at the HF/6-31G*, MP2/6-31G*, and Becke3LYP/6-31G* levels.

Thermal Reaction of 3 with Formaldehyde: Concerted vs Stepwise Mechanism. At the CASSCF level, three transition structures were located for the Diels−Alder reaction of 2-azabutadiene **3** with formaldehyde. The transition structure **TS1** (see Figure 1), corresponds to the concerted reaction pathway. The basic geometric features of this transition structure are very close to those of the transition structures located for related reactions[6,7] and show a limited asynchronicity, the length of both forming bonds being about 2.0 Å which is a typical bond-forming length for pericyclic reactions.[15]

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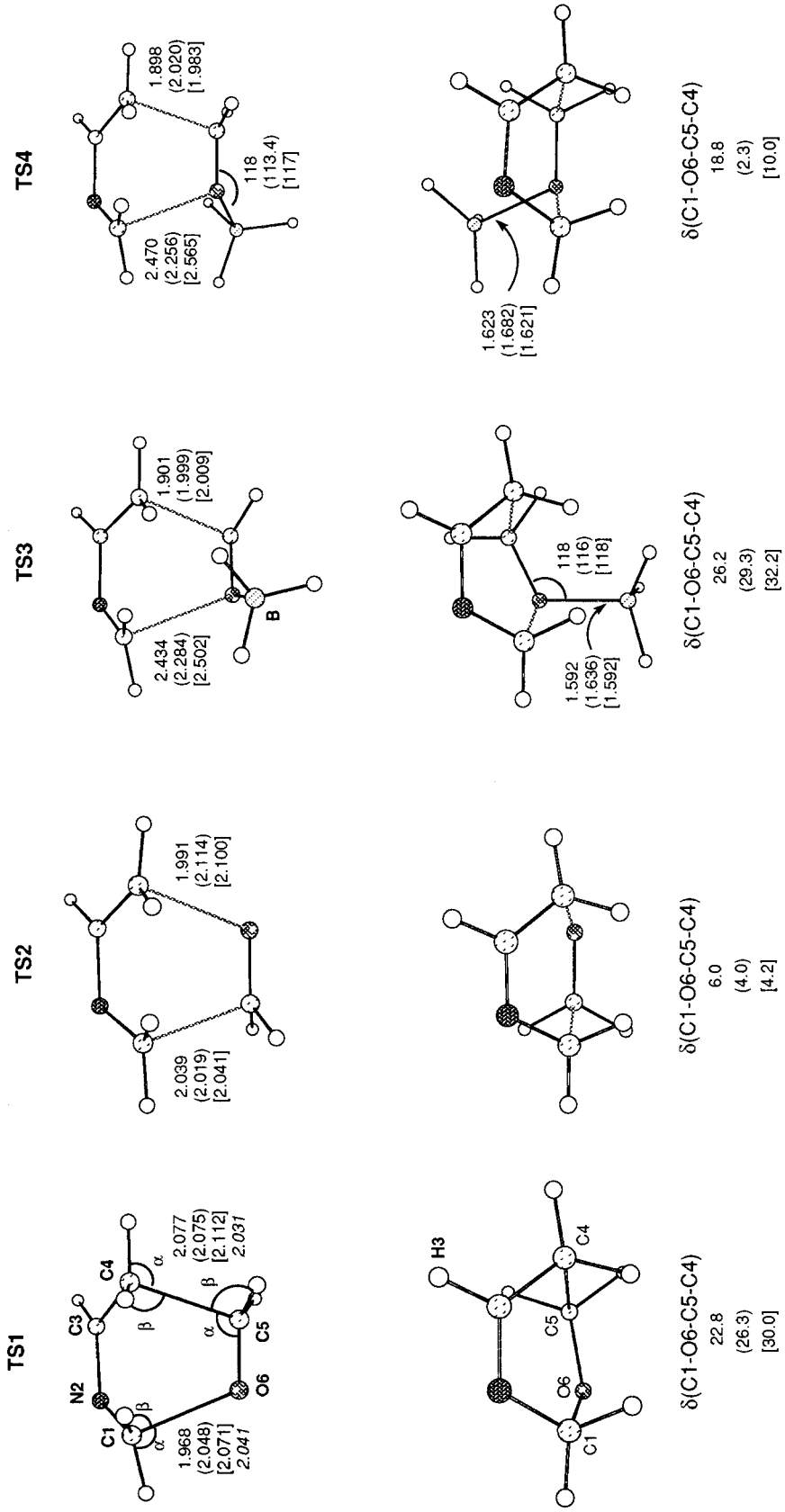


Figure 1. Transition structures for the thermal and Lewis acid catalyzed Diels−Alder reaction of 2-azabutadiene **3** with formaldehyde at the RHF/6-31G*, (MP2/6-31G*), [Becke3LYP/6-31G*], and CASSCF/6-31G* (for **TS1**, in italics) levels of theory. Lengths are in angstroms and angles in degrees.

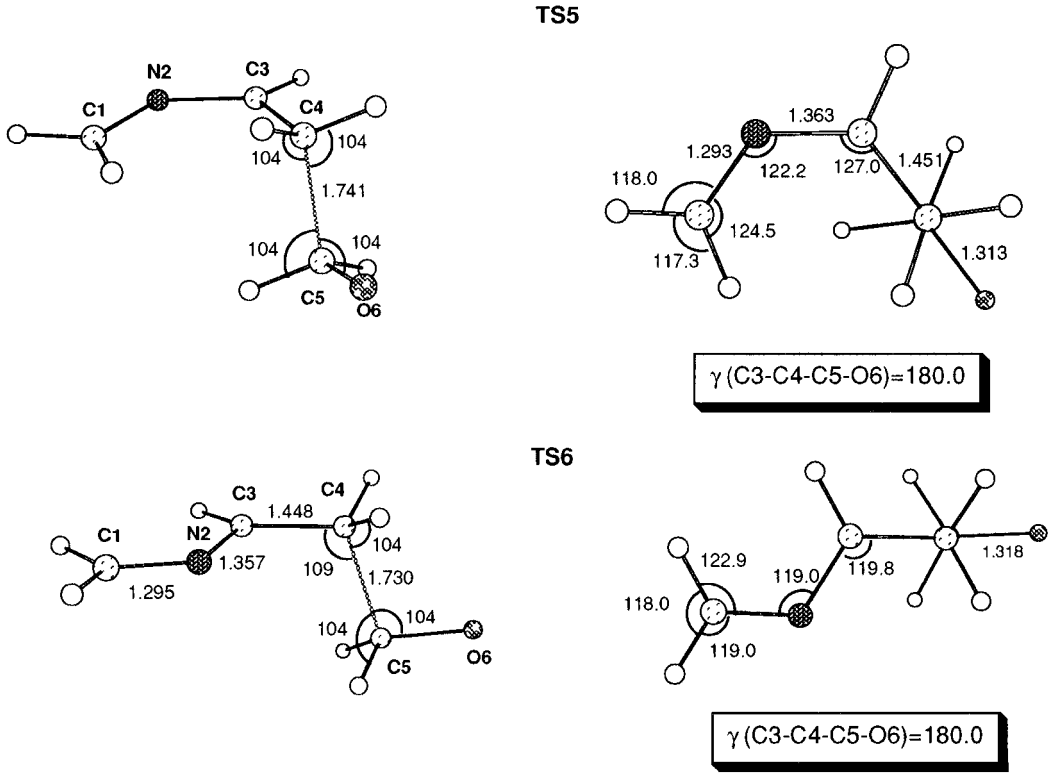


Figure 2. CASSCF/6-31G* transition structures for the stepwise Diels−Alder reaction of **3** with formaldehyde. Lengths are in angstroms and angles in degrees.

The three carbon atoms involved in the bond formation are significantly pyramidalized, as it can be seen from the bond angles shown in Figure 1 [C1: $\alpha = 100°$, $\beta = 87°$; C4: $\alpha = 110°$, $\beta = 91°$; C5: $\alpha = 108°$, $\beta = 92.7°$], which are close to the sp^3 geometry. In addition, the carbon atom of the 2-azabutadiene not involved in the formation of the new bonds is slightly pyramidal, with the attached hydrogen (H3) laying 14° out of the diene plane. This distortion allows for a better overlap between the diene π system and the new forming bonds. In **TS1** there is a significant twisting of the dienophile moiety with respect to the diene, as indicated by the value of the dihedral δ ($\delta = 11.9°$, see Figure 1). This twisting is probably caused by the electrostatic repulsion between the diene π system and the dienophile oxygen lone pairs. This phenomenon has been described before in the transition structures of other hetero Diels−Alder reactions.[6a,d]

In addition to the concerted transition structure, we found two transition structures (**TS5** and **TS6**; see Figure 2) corresponding to the stepwise addition of 2-azabutadiene **3** to formaldehyde. **TS5** is the transition structure for the C−C bond formation between the 2-azabutadiene **3**, having the *s-cis* conformation, and the formaldehyde adding *anti* to the diene. **TS6** corresponds to the C−C bond formation, with the diene having the *s-trans* conformation. In both transition structures, **TS5** and **TS6**, the dienophile oxygen O6 is *anti* to the carbon C3, the dihedral γ (see Figure 2) being 180.0°, and there is almost a perfect staggering of the substituents around the forming C4−C5 bond.

Very similar types of transition structures have been previously found in the study of the butadiene−ethylene Diels−Alder reaction.[13] In both transition structures, the two carbon atoms involved in the bond formation, C4 and C5 (see Figure 2), are significantly pyramidalized, as can be seen from the values of the bond angles, while the other atoms of the diene are in plane, showing a sp^2 geometry. On the other hand, we were unable to find a stepwise transition structure for the bond formation between the formaldehyde oxygen, O6, and the carbon C1 of the diene. At the CASSCF level all the stepwise structures corresponding to the C1−O6 bond formation collapsed to the concerted **TS1**.

Two mimima (**DI1** and **DI2**, see Figure 3), with the C4−C5 bond fully formed and the 2-azaallylic moiety completely planar, were found in the stepwise potential surface. The diradical **DI1**, with the 2-azaallylic moiety in the *s-cis* conformation, is connected with the **TS5**, while the diradical **DI2**, having the 2-azaallylic system in the *s-trans* conformation, is the intermediate corresponding to the transition structures **TS6**. In both structures **DI1** and **DI2**, the C4 and C5 carbon atoms show an sp^3 geometry

The concerted transition structure **TS1** is the most stable one, while the saddle points **TS5** and **TS6**, corresponding to the stepwise mechanism, are 5.0 and 1.6 kcal/mol higher in energy, respectively (see Table 1). Although the energetic gap between the concerted transition structure **TS1** and the stepwise *s-trans* transition structure **TS6** is quite small, it should taken into account that, as in the case of the butadiene−ethylene Diels−Alder reaction,[5b] the reaction pathway involving **TS6** and the diradical **DI2** is not a likely route to the Diels−Alder adduct. Indeed, according to the CASSCF calculations, the diradical **DI1** is 3.0 kcal/mol less stable than **DI2**, and it can be expected that the *s-trans* to *s-cis* rotational barrier in the 2-azaallylic system will be higher than the barrier for the cleavage of **DI2** *via* the transition structure **TS6**, which is predicted to be 1.1 kcal/mol.

According to these results, the reaction of **3** with formaldehyde can be predicted to be a concerted process.

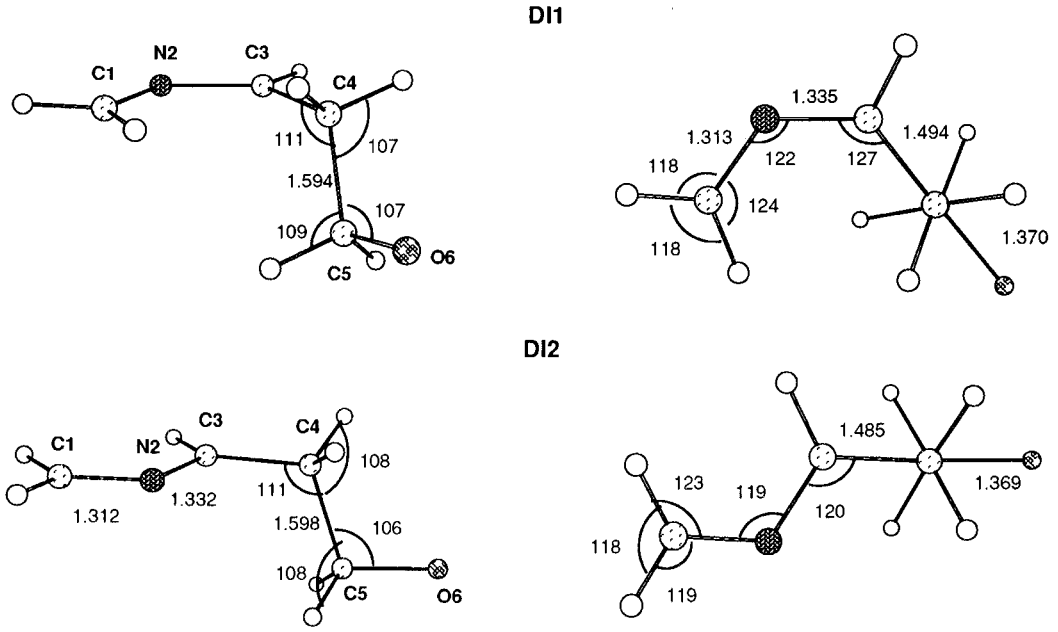


Figure 3. CASSCF/6-31G*-optimized structures of the diradical intermediates for the stepwise Diels−Alder reaction of **3** with formaldehyde. Lengths are in angstroms and angles in degrees.

Table 1. Activation Energies for the Concerted (TS1-TS4) and Stepwise (TS5-TS6) Transition Stuctures located for the Diels−Alder Reaction of 3 with Formaldehyde

theory level	TS1	TS2	TS3	TS4	TS5	TS6
HF/6-31G*	37.7	50.6	25.5	30.8	–	–
MP2/6-31G*//6-31G*	16.7	20.4	7.8	14.6	–	–
MP2/6-31G*	17.9	20.9	8.0	13.9	–	–
Becke3LYP/6-31G*	17.2	23.5	8.1	14.3	–	–
CASSCF/6-31G*	47.6	–	–	–	52.6	49.2
CASPT2F/6-31G*// CASSCF/6-31G*	19.6	–	–	–	34.8	–

However, a good determination of the concert energy will be required to take into account the correlation energy. We have found that single point energy calculations at the CASPT2F level on the CASSCF-optimized geometries (see Table 1) predict that the concerted transition structure **TS1** is 15.2 kcal/mol more stable than the stepwise transition structure **TS5**. From these data the Diels−Alder reaction of 2-azabutadiene **3** with formaldehyde is predicted to be a concerted reaction, in good agreement with the experimental evidence available.

Geometry, Regioselectivity, and Reaction Energetics. Since the concerted reaction pathway is predicted to be the favored mechanism for the Diels−Alder reaction of 2-azabutadiene **3** with formaldehyde, we carried out all the following studies on the regioselectivity, Lewis acid catalysis, and stereoselectivity at the HF/6-31G*, MP2/6-31G*, and Becke3LYP/6-31G* levels of theory. The two regioisomeric concerted transition structures for the thermal reaction of **3** with formaldehyde (**TS1** and **TS2**, see Figure 1) were optimized at the three levels of theory previously indicated. The activation energies (shown in Table 1) were evaluated also at the MP2/6-31G*//6-31G* and MP4SDTQ/6-31G*//6-31G* levels of theory.

The basic geometrical features of the HF-, MP2-, and Becke3LYP-optimized transition structures **TS1** and **TS2** are quite similar to the ones we found previously at the CASSCF level, showing a very small degree of asynchronicity. In the favored regioisomeric transition structure **TS1**, at the HF, MP2, and Becke3LYP levels, the O−C forming bond is shorter than the C−C forming bond despite of the fact that the largest LUMO coefficient of the aldehyde is at the carbon and the largest HOMO coefficient of **3** is at the C4 (see Figure 4). The degree of twisting of the dienophile moiety with respect to the diene, as shown by the value of the dihedral δ (see Figure 1) is found to be slightly higher in **TS1** than in **TS2**. It is interesting to note that the twisting is higher in **TS1** than in **TS2**, due to the additional repulsion between the lone pairs of the oxygen and the 2-azabutadiene nitrogen, which is not present in the regioisomeric transition structure **TS2**.

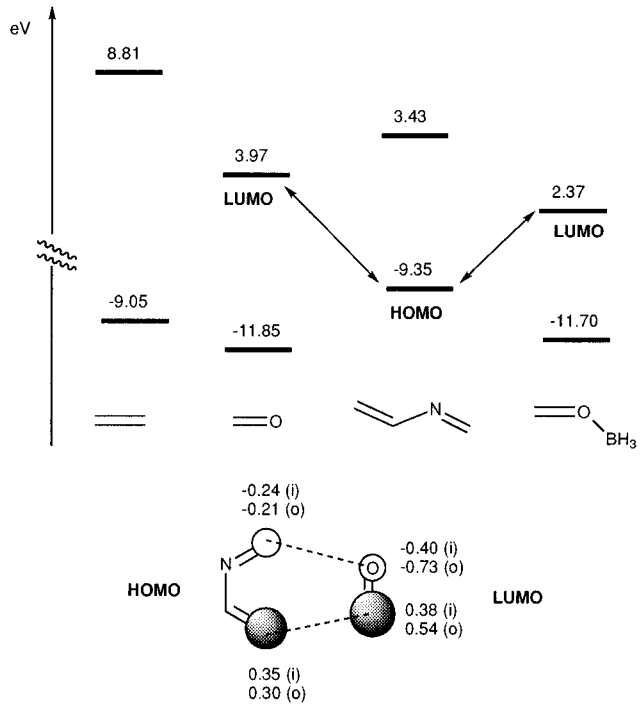


Figure 4. Frontier molecular orbital (HF/6-31G*) interactions on the Diels−Alder reaction of 2-azabutadiene **3** with formaldehyde and BH_3-complexed formaldehyde. i and o denote the inner and outer parts of the basis set.

Table 2. Reaction Energies for the Diels–Alder Reaction of 3 with Formaldehyde

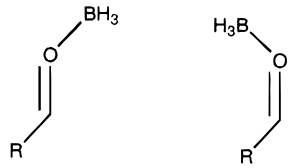
Reaction	Reaction energy		
	HF/6-31G*	MP2/6-31G*	Becke3LYP/6-31G*
3 + $H_2C{=}O$ → **4**	32.7	39.2	33.6
3 + $H_2C{=}O$ → **5**	27.8	34.4	292

From the data in Table 1 it can be seen that the regioselectivity is correctly predicted at all the theory levels considered. The relative activation energies are 12.9 (HF/6-31G*), 3.7 (MP2/6-31G*//6-31G*), 3.0 (MP2/6-31G*), 6.3 (Becke3LYP/6-31G*), and 5.7 (MP4SDTQ/6-31G*//6-31G) kcal/mol, the 1,3-regioisomer being strongly favored. On the other hand, the Diels–Alder reaction of 2-azabutadiene **3** with formaldehyde is an exothermic reaction. In Table 2 we can see the reaction energies corresponding to the formation of the two possible regioisomers: the 1,3-oxazine **4** and the 1,4-oxazine **5**. As can be seen from these data, the 1,3-oxazine derivative **4** is predicted to be the most stable one, at all levels of theory considered. However, despite of the difference in the stability of the two Diels–Alder adducts, **4** and **5**, the observed regioselectivity should be explained in terms of the lower activation energy of the transition structure leading to the 1,3-oxazine **3**. This result can be easily understood in terms of the frontier molecular orbital (FMO) theory, assuming a frontier interaction between the HOMO of the diene and the LUMO of the dienophile and taking into account the coefficients of the frontier orbitals involved (Figure 4).[16]

According to the data in Table 1, there is a good agreement in the predicted activation energy for the Diels–Alder reaction of **3** with formaldehyde at the MP2/6-31G*//6-31G*, MP2/6-31G*, and Becke3LYP/6-31G* levels of theory. Also, the activation energies computed at the MP4SDTQ/6-31G*//6-31G* level of theory (18.9 and 24.6 kcal/mol for **TS1** and **TS2**, respectively) show a good agreement with the MP2 and Becke3LYP values. It appears that the MP2 and density functional theory provides a good description of the energetics of Diels–Alder reactions, which is consistent with previous studies on other pericyclic reactions.[5,11] There are no experimental measures of the activation energies for the Diels–Alder reactions studied here, but the MP4SDTQ/6-31G* level of theory has been previously shown to be in good agreement with the experimental values for the case of the Diels–Alder reaction of butadiene with ethylene.[17]

The activation energy for the Diels–Alder reaction of 2-azabutadiene **3** with formaldehyde is lowered by 3 kcal/mol when compared with the value corresponding to the reaction of butadiene with formaldehyde (at the MP2/6-31G* level of theory)[6d] and with the cycloaddition of 2-azabutadiene with ethylene (at HF/6-31G* level of theory).[7] It is interesting to correlate this effect with the results derived from the frontier molecular orbital (FMO) analysis. It can be shown that in the thermal reaction the stronger frontier interaction takes place between the 2-azabutadiene-HOMO and the formaldehyde-LUMO (Figure 4), and this reaction can be considered a normal electron demand Diels–Alder reaction. Thus, whereas in the reaction of **3** with ethylene the total charge transfer, in the transition structure, from the ethylene-HOMO to the 2-azabutadiene-LUMO[7] is very small, in the present case, in which the formaldehyde-LUMO is strongly lowered when compared with that of the ethylene, there is a net charge transfer of 0.159 (HF/6-31G*), 0.152 (MP2/6-31G*), and 0.126 (Becke3LYP/6-31G*) electrons from the HOMO of **3** to the LUMO of formaldehyde. As the charge transfer increases, the activation energy of the reaction decreases.

Scheme 2. *Anti* and *Syn* Coordination of BH_3 to Aldehydes



Anti *Syn*

Lewis Acid Catalysis. As stated in the Introduction, the reaction of 2-azabutadiene derivatives with aldehydes usually requires the presence of boron trifluoride as a Lewis acid catalyst. In Figure 1 the two transition structures (**TS3** and **TS4**) for the Diels–Alder reaction of **3** with the formaldehyde–BH_3 complex are shown. This complex can react with **3** having the BH_3 group *endo* or *exo* orientated. From the data in Table 1 it can be noted that the predicted activation energy for the Lewis acid catalyzed reaction is strongly reduced when compared with that of the uncatalyzed reaction. The *exo*-coordinated BH_3 transition structure (**TS3**) is predicted to be favored over the *endo* one (**TS4**) at all theory levels considered. This behavior of the Lewis acids catalysts has been found before when studying other Diels–Alder reactions,[18,6d–g,7] and it can be understood in terms of a stronger interaction between the diene-HOMO and the dienophile-LUMO. In Figure 4 it can be seen that the LUMO energy of the BH_3-coordinated formaldehyde is reduced by 1.6 eV compared with formaldehyde, thus increasing the total charge transfer from the diene to the dienophile in the transition structure, which is calculated to be 0.377 (HF/6-31G*), 0.306 (MP2/6-31G*), and 0.266 (Becke3LYP/6-31G*) electrons.

The presence of the Lewis acid catalyst significantly increases the asynchronicity of the transition structures.

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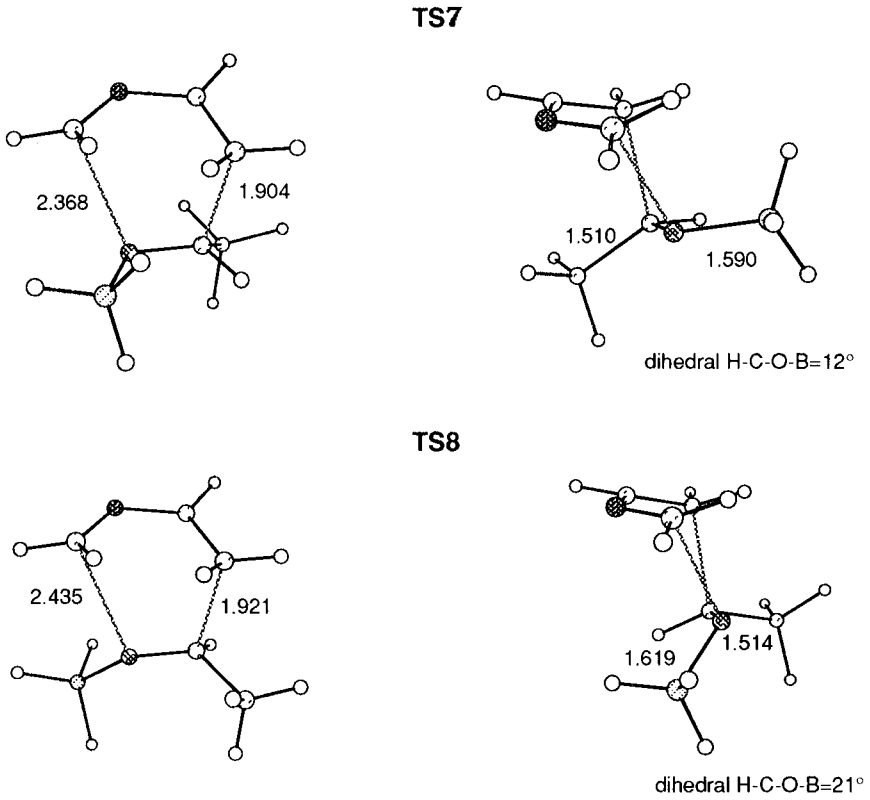

Figure 5. Transition structures for the reaction of 2-azabutadiene **3** with acetaldehyde−BH_3 complex at the RHF/6-31G* level of theory. Lengths are in angstroms and angles in degrees.

The O−C forming bond is predicted, at the three levels of theory, to be the longest one. The asynchronicity in the bond formation is also shown by the fact that the single imaginary frequency of **TS3** and **TS4** has a greater participation of the motion forming the C−C bond.

In the case of the *endo* transition structure **TS4**, the coordination of the BH_3 reduces the repulsive interaction of the *endo* lone pair of the oxygen (now involved in the coordination with the borane) with the lone pair of the nitrogen of the diene, which is reflected in the lower degree of twisting of the dienophile moiety (see the dihedral δ, in Figure 1) when compared with **TS3**. In **TS3**, there is still an oxygen *endo* lone pair, and the transition structure shows an important degree of twisting, as in **TS1**.

The preference for the *exo*-coordination of the Lewis acid catalyst can be related to the presence of steric interactions in **TS4**, between the *endo*-borane moiety and the diene fragment and to the electrostatic repulsion between the negatively charged boron atom and the diene-nitrogen lone pair (see Figure 1).

Stereoselectivity. According to the experimental results,[4] the reaction of aldehydes with 2-azabutadienes gave only the *cis*-1,3-oxazine derivatives **2** (see Scheme 1). The stereochemistry observed can be explained assuming the endo orientation of the alkyl or aryl group of the aldehyde. Previous studies have shown that the Lewis acids prefers to coordinate *anti* to the α-carbon of the aldehyde (see Scheme 2).[19] As shown before, the acid-catalyzed reaction of **3** with aldehydes is predicted to take place through a transition structure with the borane catalyst *exo*-coordinated. Taking into account both factors we can see that the preferred transition structure for the reaction of 2-azabutadienes with aldehydes should have the α-carbon of the aldehyde located *endo* and the Lewis acid located *exo*, thus leading to the observed stereochemistry. In order to test this model, two transition structures (**TS7** and **TS8**, Figure 5) were located for the reaction of **3** with BH_3-coordinated acetaldehyde. According to these calculations, the transition structure with the methyl group *endo* and the BH_3 group *exo* (**TS7**) is predicted to be favored by 5.5 kcal/mol (HF/6-31G*) and 7.9 kcal/mol (MP2/6-31G*//6-31G*) with respect to **TS8** in which the methyl group is *exo*. This result is in excellent agreement with the experimental evidence which indicates that only the 1,3-oxazine derivative **2** with stereochemistry *cis* is obtained. From the analysis of the geometry, some differences can be seen in the coordination of the borane to the aldehyde in both transition structures: the O−B bond is 0.03 Å longer in **TS8** than in **TS7** and the boron atom is more out of the plane formed by the hydrogen, carbon, and oxygen of the aldehyde in **TS8** (21°) than in **TS7** (12°). These effects can be due to the electrostatic repulsion between the negatively charged borane and the nitrogen lone pair, and this geometrical distortion could cause a poorer coordination of the Lewis acid to the aldehyde, thus reducing its ability to act as catalyst.

Summary

According to the multiconfigurational calculations, the Diels−Alder reaction of 2-azabutadiene derivatives with aldehydes can be considered a concerted cycloaddition. The concerted reaction pathway is favored by 15.2 kcal/mol over the stepwise one at the CASPT2F/6-31G*//CASSCF/6-31G* level of theory. In addition, the density functional theory appears to give a good description of the energetics of the studied reaction.

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The concerted transition structure geometries are very close at all the theory levels used and the regioselectivity of the reaction is correctly predicted and can be explained in terms of the FMO theory. The role of the Lewis acid catalyst is to lower the aldehyde-LUMO, thus increasing the charge transfer from the diene to the dienophile in the transition structure. The *anti* coordination of the Lewis acid catalyst to the aldehyde controls the stereoselectivity of the reaction. These theoretical results are in good agreement with the experimental evidences.

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Supporting Information Available: Geometries (Cartesian coordinates) and energies of the all stationary points located (14 pages). 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.

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