

Ab Initio Study of *Endo/Exo* and Diastereofacial Selectivities in Diels–Alder Reactions between Chiral Butenolides and Cyclopentadiene

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Diels–Alder reactions of cyclopentadiene with crotonolactone and β -angelica lactone have been studied using *ab initio* methods at the MP3/6-31G*/RHF/3-21G and MP2/6-31G*/RHF/6-31G* levels. The transition states corresponding to the formation of different stereoisomers and diastereoisomers have been located. The results obtained show that the correct *endo/exo* selectivity is only obtained when polarization functions are included in the basis set. However, *syn/anti* selectivity is correctly described at all levels of calculation.

Introduction

Diastereofacial selectivity on Diels–Alder reactions involving chiral dienophiles has been the subject of great interest in recent years.¹ Ortuño *et al.*² have reported several reactions of chiral α,β -butenolides with butadiene and cyclopentadiene. They have shown that these reactions proceed with high stereoselectivity and diastereoselectivity. The use of this kind of dienophile in Diels–Alder reactions plays an important role in the preparation of several natural products.³

The parent Diels–Alder reaction has been the subject of many theoretical studies.^{4–7} These have shown that reliable results can only be obtained using high level *ab initio* methods. *Ab initio* methods have also been used to study Diels–Alder reactions with unsymmetrical reactants^{8–13} and can reproduce selectivity trends. However, for reactions of chiral dienes or dienophiles, the size of the molecules involved has precluded up to now the use of these methods. The reactions of several α,β -butenolides with cyclopentadiene¹⁴ and butadiene¹⁵ have been studied using the semiempirical AM1 method. This

method predicts the formation of the adduct in which the diene attacks the less sterically hindered face of the dienophile. This result agrees with the experimental observations.²

For reactions with cyclopentadiene, in addition to the facial selectivity, two different *endo/exo* stereoisomers can be formed. The AM1 results predict the preferential formation of the *exo* adducts over the *endo* ones,¹⁴ while the experimental observations show that the *endo* isomer is the major product of the reaction.² This discrepancy on the *endo/exo* selectivity has also been observed in calculations of other Diels–Alder reactions^{9,16} and has been attributed to effects of the medium in which the real reaction takes place, which are not represented in most theoretical studies.^{14,16} Calculations including solvent effects have shown that polar solvents favor the preferential formation of *endo* adducts.^{12,16} Recently, Jorgensen *et al.*¹¹ have studied Diels–Alder reactions of cyclopentadiene with several dienophiles using *ab initio* methods at different levels of calculation. Regarding the *endo/exo* selectivity, they have observed that the results obtained depend on the level of calculation. The use of a basis set including polarization functions leads to the correct prediction of the *endo/exo* selectivity.

In this paper we report an *ab initio* study of the Diels–Alder reactions of cyclopentadiene with two α,β -butenolides: crotonolactone (2(5*H*)-furanone) and β -angelica lactone (5-methyl-2(5*H*)-furanone). Our main purpose is the study of the *endo/exo* and diastereofacial selectivities in order to rationalize the experimental observations.

Computational Details

The *ab initio* calculations have been done using the GAUSSIAN-92 program.¹⁷ For the reaction between crotonolactone and cyclopentadiene the geometries of all

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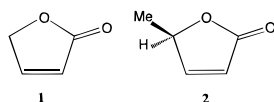
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structures have been fully optimized at the Hartree–Fock (HF) level using the 3-21G and 6-31G* basis sets.¹⁸ The vibrational frequencies have been calculated for the 3-21G structures in order to verify that transition states have one and only one imaginary frequency. The 3-21G frequencies have been used as initial guesses in the search of the 6-31G* transition states. For the reaction between β -angelica lactone and cyclopentadiene the geometry optimization has been done only with the 3-21G basis set. In order to take into account electron correlation, the energies of all the structures have been recomputed using the Møller–Plesset perturbation theory up to third order (MP3).¹⁸ The core orbitals of C and O atoms have been kept frozen in these calculations, given that the contribution of inner electrons to the correlation energy are relatively constant from one molecular environment to another.¹⁸

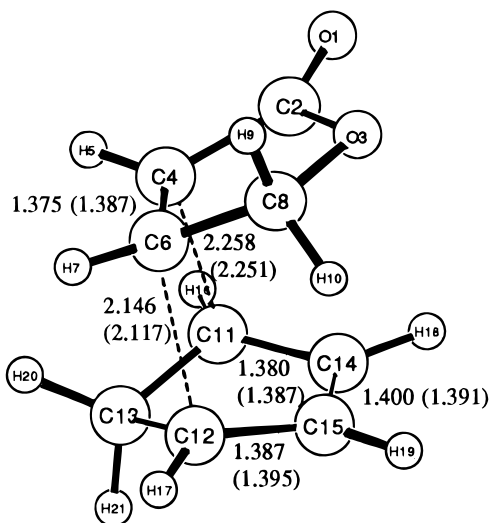
Results and Discussion

The Diels–Alder reaction of crotonolactone, **1**, with cyclopentadiene can lead to two different products: *endo* and *exo*. The structures of the transition states¹⁹ corresponding to these reactions are represented in Figure 1. For the reaction between β -angelica lactone, **2**, and

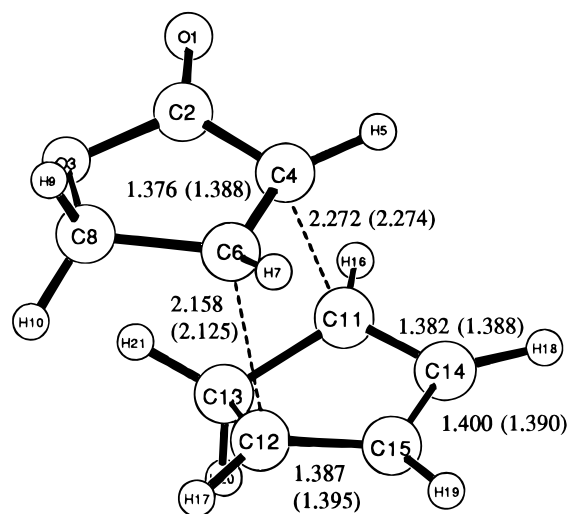


cyclopentadiene two different diastereomers can be formed: *syn* and *anti*. In this way, the reaction between **2** and cyclopentadiene can lead to the formation of four different products: *syn-endo*, *syn-exo*, *anti-endo*, and *anti-exo*. Figure 2 presents the geometries of the transition states¹⁹ corresponding to the formation of these four adducts. Table 1 presents the values of the total energies of **1**, **2**, cyclopentadiene (cp), and the transition states of the reactions of **1** and **2** with cyclopentadiene computed at several levels of calculation. Table 2 presents the values of the potential energy barriers corresponding to these reactions.

We will first discuss the results corresponding to the reaction between crotonolactone, **1**, and cyclopentadiene. For this reaction, we have located the transition states using two different basis sets. The values of the bond lengths presented in Figure 1 show that the Diels–Alder reactions between cyclopentadiene and **1** take place through nearly synchronous transition states in which the shorter of the new C–C bonds is the one involving the β carbon atom of the lactone. The 6-31G* transition states are slightly more asynchronous than the 3-21G ones. The difference between the lengths of the two forming bonds in the *endo* transition state is 0.112 Å with the 3-21G basis set, and 0.134 Å with the 6-31G* basis set. These values are smaller than the ones corresponding to the reactions of cyclopentadiene with methyl vinyl ketone, 0.181 Å (3-21G)¹² and 0.331 Å (6-31G*),¹¹ and acrolein, 0.265 Å (3-21G) and 0.339 Å (6-31G*).¹³ So, the reaction of cyclopentadiene with **1** seems to take place



a



b

Figure 1. Structures of the transition states corresponding to the formation of the *endo* (a) and *exo* (b) adducts for the reaction between **1** and cyclopentadiene. The values of the lengths of the C–C bonds directly involved in the cycloaddition obtained at the HF/3-21G level are given in angstroms. The values in parentheses correspond to the 6-31G* structures.

through transition states that are less asynchronous than the ones corresponding to the reactions of methyl vinyl ketone and acrolein.

The values of the potential energy barriers presented in Table 2 show an important dependency on the level of calculation. Upon changing from the 3-21G to the 6-31G* basis set, the potential barrier at the RHF level notably increases, due to a decrease of the basis set superposition error.²⁰ The inclusion of electron correlation at the MP2 level leads to a dramatic diminution of the barriers. In fact, the potential barriers are clearly underestimated at the MP2 level (see below). The inclusion of electron correlation up to the MP3 level leads to reasonable values that use to be within the range of experimental data.¹¹ This result shows that the correlation energy of the transition states is overestimated with respect to that of the reactants at the MP2 level. Calculations carried out

(19) Optimized geometries of all the structures are available from the authors.

(20) The basis set superposition error (BSSE) for the transition states of the reaction between **1** and cyclopentadiene has been estimated using the counterpoise method.²¹ The results obtained for the *endo* and *exo* structures are, respectively, 15.5 and 16.8 kcal/mol with the 3-21G basis set and 4.3 and 4.3 with the 6-31G* basis set.

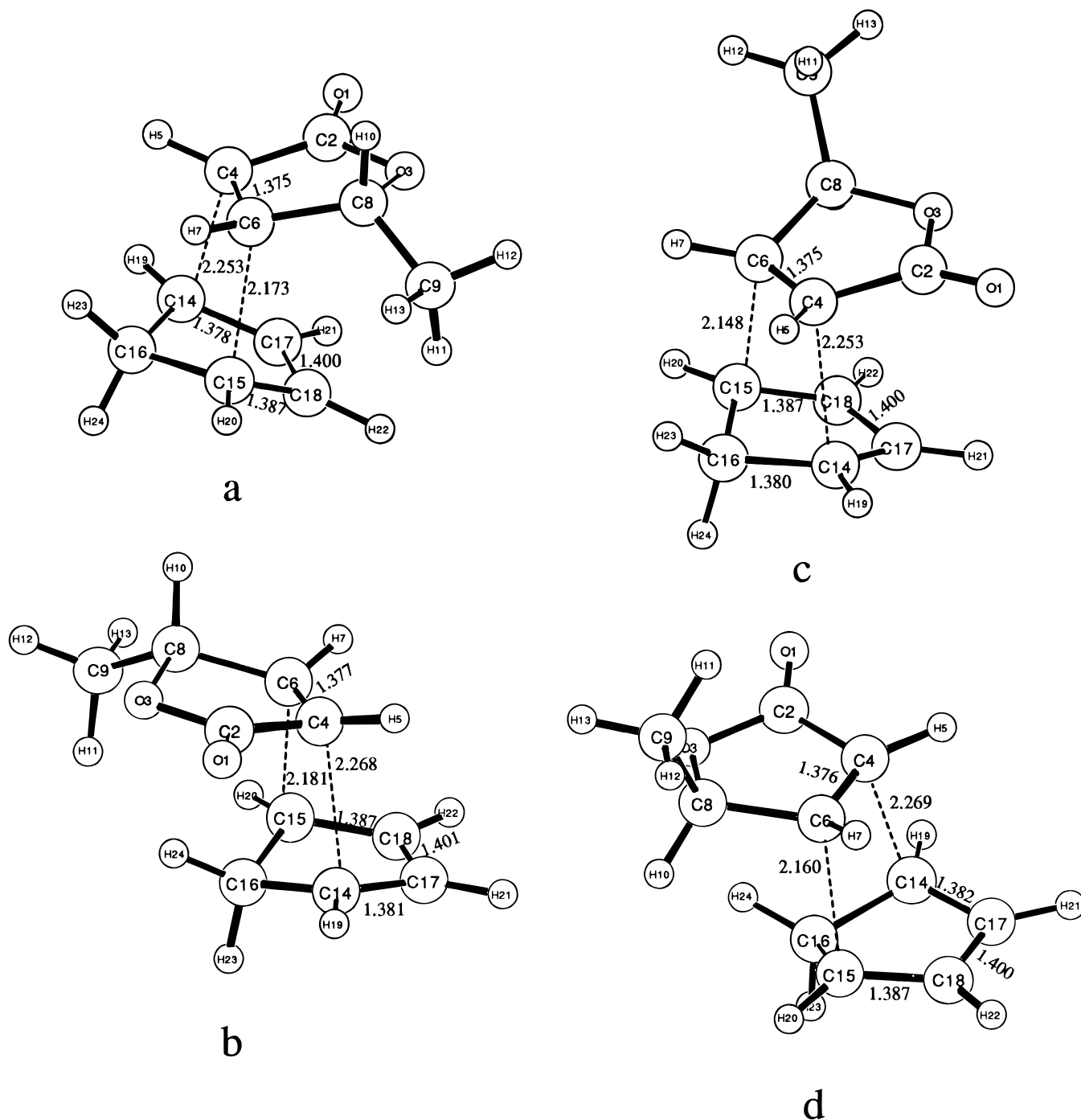


Figure 2. Structures of the transition states corresponding to the formation of the *syn-endo* (a), *syn-exo* (b), *anti-endo* (c), and *anti-exo* (d) for the reaction between **2** and cyclopentadiene. The values of the lengths of the C–C bonds directly involved in the cycloaddition are given in angstroms.

at the MP2 and higher levels of calculation^{5,7} for the reaction between butadiene and ethylene confirm this result. If we compare the values of potential barriers computed at the same level of calculation for the 3-21G and 6-31G* geometries, one can observe that the results agree within 0.7 kcal/mol. This fact justifies the use of 3-21G geometries in the study of the reaction of the β -angelica lactone, for which the geometry optimization using the 6-31G* basis set would have been very time-consuming.

Let us now compare the energy barriers corresponding to the *endo* and *exo* isomers. The values presented in Table 2 show that the predicted *endo/exo* relation is dependent on the level of calculation. Specifically, the

HF/3-21G calculation predicts the *exo* product as the kinetically most favorable. However, when a larger basis set, 6-31G*, is used, and whether or not electron correlation is taken into account, the energy ordering between the *endo* and *exo* transition states agrees with the *endo* rule.²² It is to be noted that in all these cases the difference between the *endo* and *exo* potential energy barriers changes only slightly with the level of calculation.

For the reaction between cyclopentadiene and **2**, the values of the potential energy barriers presented in Table

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Table 1. Total Energies^a Computed at Several Levels of Calculation for Cyclopentadiene, Crotonolactone, β -Angelica Lactone, and the Transition States of the Studied Diels–Alder Reactions

system	transition state	HF/3-21G// HF/3-21G	HF/6-31G*// HF/3-21G	HF/6-31G*// HF/6-31G*	MP2/6-31G*// HF/3-21G	MP2/6-31G*// HF/6-31G*	MP3/6-31G*// HF/3-21G
cp		-191.717080	-192.791376	-192.791721	-193.422783	-193.423515	-193.456032
1		-301.816149	-303.516606	-303.519369	-304.365820	-304.363968	-304.381002
1 +cp	<i>endo</i>	-493.491666	-496.245796	-496.249549	-497.781152	-497.780081	-497.806526
	<i>exo</i>	-493.492818	-496.244186	-496.248257	-497.779549	-497.778750	-497.805074
2		-340.643318	-342.545948		-343.537771		-343.559535
2 +cp	<i>syn-endo</i>	-532.310062	-535.280303		-536.950408		-536.984404
	<i>syn-exo</i>	-532.313570	-535.280357		-536.950036		-536.983969
	<i>anti-endo</i>	-532.318412	-535.286098		-536.956056		-536.989228
	<i>anti-exo</i>	-532.319438	-536.284628		-536.954507		-536.987806

^a In au.**Table 2. Potential Energy Barriers^a Computed at Several Levels of Calculation for the Reactions of Crotonolactone and β -Angelica Lactone with Cyclopentadiene**

dienophile	transition state	HF/3-21G// HF/3-21G	HF/6-31G*// HF/3-21G	HF/6-31G*// HF/6-31G*	MP2/6-31G*// HF/3-21G	MP2/6-31G*// HF/6-31G*	MP3/6-31G*// HF/3-21G
1	<i>endo</i>	26.1	39.0	38.6	4.7	4.6	19.1
	<i>exo</i>	25.4	40.0	39.4	5.7	5.4	20.0
2	<i>syn-endo</i>	31.6	35.8		6.4		19.6
	<i>syn-exo</i>	29.4	35.7		6.6		19.8
	<i>anti-endo</i>	26.3	32.1		2.8		16.5
	<i>anti-exo</i>	25.7	33.0		3.8		17.4

^a In kcal mol⁻¹.**Table 3. Activation Enthalpies, Entropies and Gibbs Energies Computed at 298.15 K and 1 atm for the Reactions of Dienophiles **1** and **2** with Cyclopentadiene^a**

dienophile	transition state	ΔH^\ddagger ^b	ΔS^\ddagger ^c	ΔG^\ddagger ^b
1	<i>endo</i>	20.0	-47.8	34.2
	<i>exo</i>	21.1	-48.5	35.6
2	<i>syn-endo</i>	20.6	-47.8	34.9
	<i>syn-exo</i>	20.9	-49.3	35.6
	<i>anti-endo</i>	17.4	-48.1	31.7
	<i>anti-exo</i>	18.5	-48.7	33.0

^a Computed from the MP3/6-31G*//HF/3-21G electronic energies and the HF/3-21G vibrational frequencies scaled by 0.9. ^b In kcal mol⁻¹. ^c In cal K⁻¹ mol⁻¹.

2 show the same kind of dependence on the level of calculation. The correct *endo* preference is predicted at all levels of calculation except HF/3-21G. Regarding the *syn/anti* selectivity one can observe a clear preference for the *anti* products in all cases, in excellent agreement with the experimental results.² Regarding the geometry of the transition states, the degree of asynchronicity is very similar to that obtained for the transition states corresponding to the reaction of **1**.

We have computed the values of activation enthalpies, entropies, and Gibbs energies corresponding to the studied reactions.¹⁸ We have used the potential energy barriers computed at the MP3/6-31G*//HF/3-21G level along with the HF/3-21G harmonic frequencies. This frequencies have been scaled by 0.9.¹⁸ The results obtained are presented in Table 3.

The inclusion of the zero-point energy and of thermal contributions to the barriers leads to a small increase in the difference between the *endo* and *exo* transition states. Moreover, one can observe that the activation entropy corresponding to the formation of the *exo* adduct is slightly more negative than that corresponding to the *endo* adduct. As a consequence, the differences between *endo/exo* Gibbs activation energies are larger than the ones corresponding to the potential energy barriers and to the activation enthalpies. On the contrary, the inclusion of the zero-point vibrational energies, thermal contributions to the energy, and entropy do not change the difference between *syn/anti* barriers. The differences

between computed Gibbs activation energies corresponding to *exo* and *endo* transition states of the reactions of **1** and **2** (*anti*) with cyclopentadiene are 1.4 and 1.3 kcal mol⁻¹, respectively. These values lead to a ratio between *endo* and *exo* rate constants of 9–10 at 298 K. This value is larger than the ratio of *endo* and *exo* isomers, 3–2.5: 1,^{2c} experimentally observed for reactions of several chiral butenolides with cyclopentadiene in a temperature range between 353 and 393 K. The observed *endo/exo* selectivity has been shown to be temperature dependent, the ratio between *endo* and *exo* products decreasing with temperature. Regarding the diastereofacial selectivity, the difference between computed Gibbs activation energies corresponding to the *syn-endo* and *anti-endo* transition states for the reaction between **2** and cyclopentadiene is 3.2 kcal mol⁻¹, leading to a ratio between *anti* and *syn* rate constants of 222, which is consistent with the complete *anti* stereofacial selectivity experimentally observed.^{2c}

The results presented up to now show that the correct *endo* preference is obtained with proper level of calculation. This fact does not exclude other contributions to the experimentally observed preference for *endo* products. Real Diels–Alder reactions take place in solution or in gas phase at a certain pressure, while the theoretical calculations presented here would correspond to a extremely low pressure. Medium effects could affect the relative stability of *endo* and *exo* transition structures.

The product distributions of Diels–Alder reactions can be affected by pressure.²³ The molecular volumes of *endo* and *exo* transition structures can be theoretically calculated²⁴ and so the difference between *endo* and *exo* activation volumes can be estimated. This difference is -1.3 cm³ mol⁻¹ for the reaction of **1** with cyclopentadiene and -0.5 cm³ mol⁻¹ for the reaction corresponding to **2** (*anti*). In both cases, the *endo* transition state presents a smaller molecular volume than the *exo* one. This result is in good agreement with experimental observations, in

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Table 4. Dipole Moment and Charge Transfer to the Dienophile on the Transition States of the Reactions between Lactones and Cyclopentadiene

lactone	transition state	μ^a	t^b
1	<i>endo</i>	6.004	0.127
	<i>exo</i>	5.727	0.124
2	<i>syn-endo</i>	5.876	0.124
	<i>syn-exo</i>	5.602	0.119
	<i>anti-endo</i>	5.872	0.122
	<i>anti-exo</i>	5.602	0.119

^a In Debyes. ^b Computed from the Mulliken Population Analysis, in atomic units.

which the *endo* product is generally favored at high pressures.²³ Regarding the diastereofacial selectivity in the reaction between **2** and cyclopentadiene, the value of the molecular volume computed for the *syn-endo* transition state is 0.5 cm³ mol⁻¹ smaller than the value corresponding to the *anti-endo* transition state. Thus, facial selectivity should decrease at high pressure.

Solvent effects also play a role in the selectivity of Diels–Alder reactions, increasing the *endo/exo* selectivity.²⁵ Theoretical calculations^{12,16} have shown that polar solvents stabilize with preference the *endo* transition state due to its higher electric dipole moment. Table 4 presents the values of the dipole moment and of the charge transfer to the dienophile corresponding to the transition structures of the studied reactions.

We can observe that *endo* transition states have larger values of the dipole moment than the *exo* transition states. The dipole moment of the isolated crotonolactone molecule is 5.622 D at the HF/3-21G level, pointing in the opposite direction of the COO group. On the other hand, cyclopentadiene has a small dipole moment (0.385 D with the 3-21G basis set) pointing toward the methylene group. These dipole moments are parallel in the *endo* transition state, leading to a higher overall dipole moment. The presence of solvent molecules would stabilize with preference the *endo* transition state, thus leading to an increase of the *endo/exo* selectivity.^{7,8} The presence of other diene or dienophile molecules in a gas phase medium at high pressure could be considered to produce the same kind of effect as a solvent, since molecular interactions would stabilize with preference structures having larger dipole moments.

The direction of the dipole moment of the transition states is mainly determined by the COO group, with a very small contribution in the direction of the approaching cyclopentadiene molecule. This fact is consistent with the small value of charge transfer between diene and dienophile computed from the Mulliken population analysis. This charge transfer is only slightly larger for the *endo* transition state than for the *exo* one.

One of the most usual explanations offered for *endo* selectivity is that secondary overlap favors the *endo* transition state.²² An analysis of the Mulliken overlap populations between atomic orbitals of carbon atoms of cyclopentadiene and crotonolactone does not show any significant difference between *endo* and *exo* transition states. Regarding the geometry parameters presented in Figures 1 and 2, one can observe that the lengths of the two forming C–C bonds are slightly smaller for the *endo* transition states than for the *exo* ones. This fact

seems to indicate that stabilizing interactions bring both reactant molecules closer to each other for the *endo* transition states. However, other intermolecular geometry parameters do not follow the same trend. The 3-21G computed values of the distance between C2 and C11 (see Figure 1) at the *endo* and *exo* transition states of the reaction between cyclopentadiene and crotonolactone are 2.856 Å and 2.843 Å, respectively, while the values of the distance between C8 and C12 are 2.947 Å for the *endo* transition state and 2.904 Å for the *exo* one. Similar results are obtained with the 6-31G* basis set. These results seem to indicate that repulsive interactions between both reactant molecules should also be more important for the *endo* transition states. In fact, the overlap between the HOMO of the diene and the LUMO of the dienophile is maximized when the diene and dienophile molecules approach each other in an *endo* orientation, but, at the same time, the overlap between occupied orbitals of both molecules is also favored. The observed *endo* selectivity indicates that the stabilizing interactions can overcome the larger repulsive interactions involved in *endo* transition states.

One of the reviewers has attracted our attention to the value of the dihedral angle between the forming bonds at the transition states. Both in *endo* and *exo* transition states, there is a slight deviation from planarity for the four carbon atoms involved in these bonds. The 3-21G values of the C4–C6–C12–C11 dihedral angle (see Figure 1) are, respectively, -2.0° and 2.7° for the *endo* and *exo* transition states of the reaction between crotonolactone and cyclopentadiene. In both cases, this slight distortion approaches the carbonyl group of crotonolactone to the C11 atom of cyclopentadiene.

Regarding the *syn/anti* selectivity, the values of the dipole moment and charge transfer presented in Table 4 do not show any significant difference between *syn* and *anti* transition states. The difference between *syn* and *anti* transition states could be attributed only to steric effects. The steric hindrance produced by the methyl group of β -angelica lactone when cyclopentadiene approaches the *syn* face is the responsible of the higher energy barrier. Single point calculations on the *endo* transition state of the reaction between **1** and cyclopentadiene replacing one of the methylenic H atoms by a methyl group leads to an energy difference of 18.5 kcal/mol between *syn* and *anti*. This steric repulsion causes the values of the lengths of the forming bond closer to the methyl group (C6–C15 in Figure 2) to be slightly larger in the *syn* transition states, so that the difference between the energies of the *syn* and *anti* optimized transition states is notably smaller. Other geometry parameters present values with significant differences between *syn* and *anti* transition states. The distance between C8 and C18 (see Figure 2) is 3.208 Å for the *syn-endo* transition state and 2.998 Å for the *anti-endo* one. Finally, the values of the C4–C6–C15–C14 dihedral angle are 3.6° and -1.9° for the *syn-endo* and *anti-endo* transition states, respectively. These results show that the steric repulsion between both reactant molecules is transferred into changes in the geometries of the transition states.²⁶ The values of the C8–C18 distance and of the C4–C6–C15–C14 dihedral angle corresponding to the *anti-endo* transition state are very similar to the values of the C8–C15 distance and C4–C6–C12–C11

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dihedral angle corresponding to the *endo* transition state of the reaction of crotonolactone (see above). On the contrary, the values corresponding to the *syn-endo* transition state significantly change in order to minimize the steric repulsion caused by the methyl group.

Concluding Remarks

We have studied the reactions of crotonolactone and β -angelica lactone with cyclopentadiene. The formation of *endo* adducts involves smaller energy barriers than the formation of *exo* adducts. However, this result is only obtained when a basis set with polarization functions is used. The *endo/exo* selectivity is due to more favorable

stabilizing interactions in *endo* transition states. Regarding the *syn/anti* diastereoselectivity, we have found that the formation of *anti* products, in which the attack of cyclopentadiene takes place in the less sterically hindered face of the lactone, is more favorable than the formation of *syn* adducts. The *syn/anti* selectivity is correctly predicted at all levels of calculation.

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