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Ab Initio Study of Stereo- and Regioselectivity in the Diels−Alder Reaction between 2-Phenylcyclopentadiene and α-(Methylthio)acrylonitrile

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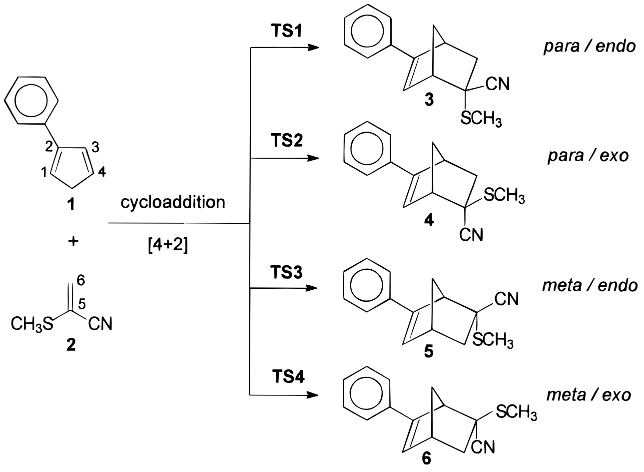
Ab initio molecular orbital calculations have been used to investigate the Diels−Alder reaction between 2-phenylcyclopentadiene and α-(methylthio)acrylonitrile. Geometry optimizations were performed with the RHF/3-21G, RHF/3-21G*, and RHF/6-31G* calculations while the correlation energy has been calculated at MP2 and MP3 levels. Four asynchronous transition structures corresponding to the formation of different stereoisomers and regioisomers associated with the four reaction channels have been located. The observed *endo*/*exo* stereoselectivity and *para*/*meta* regioselectivity are correctly described at all levels of calculation, and the calculated activation energies reflect accurately the relative reactivities along the four reactive channels. However, the enthalpies of activation reach good accord with experimental results only when the correlation energy is included at the MP3 level. The theoretical results point out that the regioselectivity is controlled by the presence of a phenyl group on C2 carbon atom of the diene system while the stereoselectivity is controlled by a favorable secondary orbital overlap between the lone pair of the sulfur atom located in the dienophile fragment and the π system of the diene at the *endo* transition structures.

Introduction

The Diels−Alder cycloaddition has been demonstrated to be a powerful synthetic method for multiple carbon−carbon bond formation in a stereo- and regioselective manner.[1] This reaction involving asymmetric dienophiles has been the subject of several theoretical and experimental studies. In particular, Bernard-Henriet and Chanon[2] have reported the reaction of 2-phenylcyclopentadiene, **1**, with α-(methylthio)acrylonitrile, **2**, as a part of a research program devoted to the development of a convenient approach to check the presence of radical intermediates during organic reactions.[3] This reaction[2] exhibits high regio- and stereoselectivity, to give a 85:15 mixture of the *para* adducts *endo*/*exo*, **3** and **4**, respectively; while the *meta* adducts *endo*/*exo*, **5** and **6**, have not been observed. Scheme 1 illustrates the different reactive channels and the atoms numbering.

Over the last years, substantial progress has been made in the theoretical study of Diels−Alder reactions.[4] *Ab initio* methods have been used to study Diels−Alder reactions with unsymmetrical reactants[5,6] and can reproduce selectivity trends. Jorgensen et al.[7] have studied the 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. In addition, Oliva et al.[8] have studied the Diels−Alder reaction between butenolides and cyclopentadiene, showing that the use of basis sets including polarization functions is essential to the correct prediction of the *endo*/*exo* selectivity.

Scheme 1



In this paper we report an *ab initio* study of the Diels−Alder reaction of 2-phenylcyclopentadiene, **1**, with α-(methylthio)acrylonitrile, **2**, in an attempt to understanding the competitive pathways of this reaction. Our main purpose is the study of the *endo*/*exo* stereoselectivity and the *para*/*meta* regioselectivity in order to explain the experimental results.[2]

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Table 1. Total Energies (au) Computed at Several Levels of Calculations for the Diels−Alder Reaction between 2-Phenylcyclopentadiene and α-(Methylthio)acrylonitrile

	HF/3-21G	HF/3-21G*	HF/6-31G*	MP2/3-21G*//-HF/3-21G*	MP2/6-31G*//-HF/6-31G*	MP3/3-21G*//-HF/3-21G*	MP3/3-21G*//-HF/6-31G*
1 + 2	−1023.183554	−1023.292160	−1028.654138	−1024.835781	−1030.824262	−1024.896154	−1024.895642
TS1	−1023.144861	−1023.253914	−1028.598583	−1024.835394	−1030.823699	−1024.878239	−1024.876188
TS2	−1023.144459	−1023.252844	−1028.597779	−1024.834160	−1030.822408	−1024.877293	−1024.875199
TS3	−1023.140753	−1023.249938	−1028.593842	−1024.833609	−1030.821375	−1024.876088	−1024.874322
TS4	−1023.140526	−1023.248747	−1028.592829	−1024.832491	−1030.820142	−1024.875287	−1024.873554

Computing Methods

All geometry optimizations and gas phase energy calculations were carried out with the Gaussian 94 suite of programs.[9] Unless otherwise specified, all geometries of the reactants and transition structures (TSs) have been fully optimized at the restricted Hartree−Fock (RHF) level with the 3-21G, 3-21G*, and 6-31G* basis sets.[10] The sulfur atom of the thioether group plays an important role in the stereoselectivity of this reaction; thus we have used the 3-21G* basis set, which includes the polarization d functions for the second row elements (sulfur atom). Previous studies of Diels−Alder reactions have indicated that the activation energies calculated at the HF level of theory are too large while the MP2 calculations underestimate it.[6,7,11−14] However, MP3 calculations are in quite reasonable agreement with the experimental activation energy values.[7] Therefore, we have carried out single point energy calculations at MP2/3-21G*//RHF/3-21G*, MP2/6-31G*//RHF/6-31G*, MP3/3-21G*//RHF/3-21G*, and MP3/3-21G*//RHF/6-31G* levels in order to analyze the effect of the electron correlation energy in the potential barriers.[10]

The localization of the TSs was achieved using a simple algorithm developed by us.[15] The optimizations were carried out using the Berny analytical gradient optimization method.[16] Finally, the nature of each stationary point was established by calculating analytically and diagonalizing the matrix of the energy second derivatives to determine the number of imaginary frequencies, zero for local minima and one for a TS. The transition vector,[17] i.e. the eigenvector associated to the unique negative eigenvalue of the force constants matrix, has been characterized.

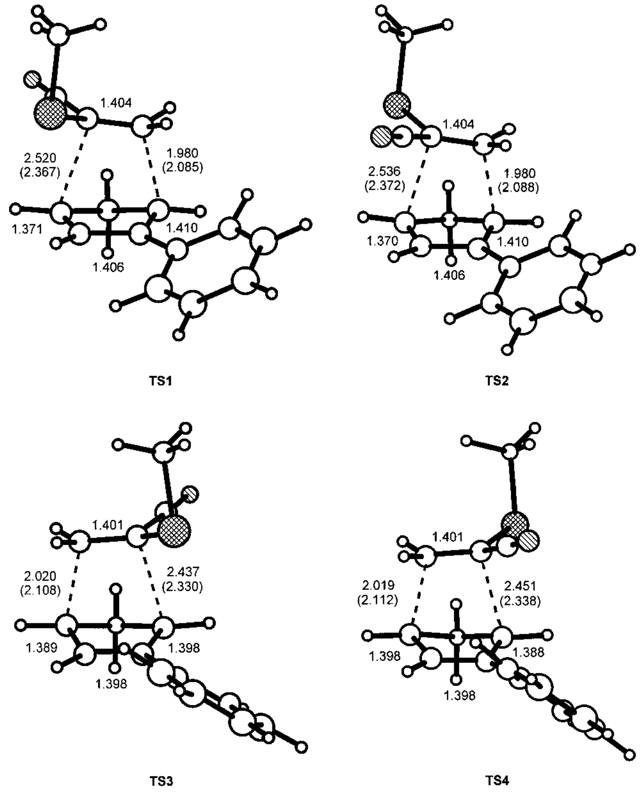

Figure 1. HF/6-31G* transition structures corresponding to the Diels−Alder reaction between 2-phenylcyclopentadiene and α-(methylthio)acrylonitrile. The distance of the forming C−C bonds are in angstroms. The values in parentheses correspond to the HF/3-21G* structures.

Results and Discussion

The Diels−Alder reaction of 2-phenylcyclopentadiene, **1**, with α-(methylthio)acrylonitrile, **2**, can lead to four different products: *para*/*endo*, **3**, *para*/*exo*, **4**, *meta*/*endo*, **5**, and *meta*/*exo*, **6**, adducts. The geometries of the transition structures[18] corresponding to the formation of these four adducts: **TS1**, **TS2**, **TS3**, and **TS4**, respectively, are depicted in Figure 1. In Table 1, the values of the total energies for reactants and the four transition structures computed at several levels of calculation are given. Table 2 presents the values of the potential energy barriers and relative energies corresponding to transition structures of these reactions.

The values of the selected bond lengths represented in Figure 1 show that the Diels−Alder reactions between 2-phenylcyclopentadiene, **1**, and α-(methylthio)acrylonitrile, **2**, take place along asynchronous transition structures in which the shorter of the forming bonds is the one involving the *β* carbon of α-(methylthio)acrylonitrile. The geometrical values obtained with the 3-21G and 3-21G* basis sets are similar; however, the 6-31G* transition structures are more asynchronous than the 3-21G and 3-21G* ones. The differences between the forming bonds, C1−C6 and C4−C5 for the *para* transition

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Table 2. Potential Energy Barriers (ΔE) and relative energies ($\Delta\Delta E$) (kcal/mol) for the Diels−Alder Reaction between 2-Phenylcyclopentadiene and α-(Methylthio)acrylonitrile

	HF/3-21G		HF/3-21G*		HF/6-31G*		MP2/3-21G*//HF/3-21G*		MP2/6-31G*//-HF/6-31G*		MP3/3-21G*//-HF/3-21G*		MP3/3-21G*//-HF/6-31G*	
	ΔE^a	$\Delta\Delta E^b$	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$
TS1	24.28	0.00	24.00	0.00	34.86	0.00	0.24	0.00	0.35	0.00	11.24	0.00	12.21	0.00
TS2	24.53	0.25	24.67	0.67	35.37	0.50	1.02	0.77	1.16	0.81	11.84	0.59	12.83	0.62
TS3	26.86	2.58	26.49	2.49	37.84	2.97	1.36	1.12	1.81	1.46	12.59	1.35	13.38	1.17
TS4	27.00	2.72	27.24	3.24	38.47	3.61	2.06	1.82	2.58	2.23	13.09	1.85	13.86	1.65

[a] Relative to **1** + **2**. [b] Relative to **TS1**.

Table 3. Dipole Moment (Debye) and Charge Transfer (au) to the Dienophile on the Transition Structures for the Diels−Alder Reaction between 2-Phenylcyclopentadiene and α-(Methylthio)acrylonitrile

		q^a
TS1	6.3	0.25
TS2	5.3	0.22
TS3	5.1	0.22
TS4	4.5	0.21

[a] Charges calculated from CHELPG method.

structures **TS1** and **TS2**, and C1−C5 and C4−C6 for the *meta* transition structures **TS3** and **TS4** are, respectively: 0.282, 0.284, 0.222, and 0.226 Å (3-21G results); 0.328, 0.342, 0.263, and 0.289 Å (3-21G* results); and 0.540, 0.556, 0.417, and 0.432 Å (6-31G* results). These values show that **TS1** and **TS2** are more asynchronous than **TS3** and **TS4**.

The values of the potential energy barrier presented in Table 2 show an important dependency on the level of calculation. Upon changing from 3-21G or 3-21G* to 6-31G* basis set level, the potential barrier increases. The inclusion of electron correlation energy at the MP2 level leads to a significant decrease of the energy barriers, while the inclusion of electron correlation energy up to the MP3 level leads to reasonable values of the activation parameters.[7] This fact shows that MP2 calculations overestimate the effect of the electron correlation energy on the transition structures with respect to that of the reactants, in agreement with previous studies of related Diels−Alder reactions.[6,7,11−14] Bach et al.[11] have demonstrated that convergence to experimental activation energy for the reaction of ethylene with 1,3-butadiene could be achieved by using a basis set with polarization functions and extensive treatment of the correlation energy (MP4SDTQ/6-31G*). However, this level is only applicable with practical purpose to small systems. Our computer capabilities only allow us to study the present system at MP3 level, thus obtaining a better estimation of activation enthalpies.

The relative energies between the four transition structures shown in Table 2 reveal that the relations *endo*/*exo* and *meta*/*para* are only slightly dependent on the computing level. These data are in good agreement with the stereo- and regioselectivity observed to give the *para* regioisomers more stable (1.2−3.6 kcal/mol) than the *meta*, while the *endo* stereoisomers are more stable (0.3−0.8 kcal/mol) than the *exo* ones.

The presence of two electron-withdrawing groups, cyano and methylthio substituents, on the dienophile system, and an electron-releasing group, a phenyl substituent, on the diene system, promotes the charge transfer process from the dienophile to the diene system (Table 3). The charge transfer is only slightly larger for the *para* transition structures **TS1** and **TS3** (0.25 and 0.22 au, respectively) than for the *meta* transition structures, **TS2** and **TS4** (0.22 and 0.21 au, respectively). At the transition structures, the positive charge in the diene fragment is centered on the C2 atom, while the negative charge is located on the C5 atom of the dienophile system, in the four transition structures. The phenyl group on the C2 atom allows the delocalization of the positive charge generated at the transition structures on the cyclopentadiene ring, and this effect is more pronounced for the *para* transition structures. This stabilizing effect of the phenyl group on the transition structures allows us to explain the *para*/*meta* regioselectivity experimentally obtained.[2]

An analysis of the frontier molecular orbitals in the reactants shows that 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. Hehre et al.[19] and Craig and Stone[20] have discussed the shortcomings of FMO theory in rationalizing the regio and stereoselectivity of the Diels−Alder reactions. However, an analysis of the HOMO-1 at the transition structures shows that a significant contribution to the smaller activation energy for the *endo* transition structures compared with the corresponding *exo* transition structures is a result of a favorable interaction between the lone pairs located on the sulfur atom and the π system of the diene fragment. This fact has been offered previously by Sauer and Sustmann[21] to explain the favorable *endo* reactive channels for related Diels−Alder reactions and can explain the *endo*/*exo* stereoselectivity found experimentally.[2]

Regarding the geometric parameters presented in Figure 1, one can observe that the lengths of the C1−C6 forming bonds are slightly smaller for the *para* transition structures, **TS1** and **TS2**, than the C4−C6 forming bonds for the *meta*, **TS3** and **TS4**; while an opposite trend is found for the C4−C5 and C1−C5 forming bonds. These facts seem to indicate that the stabilizing interactions bring both reactant molecules close to each other for the *para* transition structures, **TS1** and **TS2**, in which the phenyl group is located on C2 atom of the diene system, and the *endo* transition structures, **TS1** and **TS3**, in which the sulfur atom is located over the diene system moiety.

We have estimated the values of activation enthalpies, entropies, and Gibbs energies corresponding to the four reactive channels by means of the potential energy barriers computed at the MP3/3-21G*//RHF/3-21G* level along with the RHF/3-21G* harmonic frequencies. These

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Table 4. Activation Enthalpies (kcal/mol), Entropies (cal/K mol), and Gibbs Energies (kcal/mol) Estimated at 298.15 K and 1 atm for the Diels−Alder Reaction between 2-Phenylcyclopentadiene and α-(Methylthio)acrylonitrile[a]

	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
TS1	11.7	−25.4	18.6
TS2	12.3	−25.0	19.1
TS3	12.9	−25.9	20.0
TS4	13.4	−25.4	20.4

[a] Estimated from MP3/3-21G*//HF/3-21G* electronic energies and the HF/3-21G* vibrational frequencies scaled by 0.9.

frequencies have been scaled by 0.9.[10,22] The enthalpy and entropy changes are calculated from standard statistical thermodynamic formulas.[10] The results are presented in Table 4. The inclusion of the zero point energy and the thermal contributions to the barriers lead to a small decrease in the difference between the *para*/*meta* transition structures, while the activation entropy of the *endo* transition structures is slightly more negative than the corresponding to the *exo* transition structures. As a consequence, the differences between estimated Gibbs activation energies corresponding to *para*/*endo* and *para*/*exo* transition states of the reaction of 2-phenylcyclopentadiene and α-(methylthio)acrylonitrile is 0.5 kcal/mol, while this difference between the *meta*/*endo* and *meta*/*exo* is 0.4 kcal/mol. These values lead to a ratio between the *para*/*endo* and *para*/*exo* rate constants of 2.3 at 298.15 K. Regarding the regioselectivity, the differences between estimated Gibbs activation energies corresponding to the *para* and *meta* transition structures lead to a ratio between the *para* and *meta* rate constants in the range 10.0−12.0, which is consistent with the complete *para* regioselectivity experimentally observed.[2]

The results presented up to now show that the correct *para*/*meta* and *endo*/*exo* preferences are obtained with our calculations in gas phase. However, the experimental results[2] are obtained in dioxane solvent. Medium effects on Diels−Alder reaction are well known,[23] and they can contribute to the experimentally observed preferences. Correlations with empirical solvent parameters have been discussed for the reaction rates, *para*/*meta* regioselectivity, and *endo*/*exo* selectivity.[24] In particular, solvent effects can play a role in the selectivity of Diels−Alder reactions, increasing the *endo*/*exo* selectivity.[25] Theoretical calculations[26] have shown that polar solvents stabilize with preference the *endo* transition structures due to its higher electric dipole moment. The dipole moment calculation is independent of the Mulliken population analysis and hence provides an alternative view of the degree of charge separation. Table 3 presents the values of the dipole moments corresponding to the four transition structures. We can observe that the *para* transition structures have larger values of the dipole moment than the *meta* transition structures, and that the *endo* transition structures have also large values of the moment dipole than the *exo* transition structures. Thus, the presence of polar solvent molecules would increase the *para*/*meta* stereoselectivity and the *endo*/*exo* regioselectivity.

Finally, the experimental Diels−Alder reaction takes place in solution, while the theoretical calculations presented here correspond to gas phase conditions. Medium effects could affect the relative stability of the *endo*/*exo* transition structures. Thus, the product distributions of Diels−Alder reactions can be affected by pressure.[27] The molecular volumes[28] of the four transition structures have been obtained, and the corresponding values are **TS1** (176.57 cm^3/mol), **TS2** (196.27 cm^3/mol), **TS3** (174.15 cm^3/mol), and **TS4** (238.59 cm^3/mol). The *endo* transition structures present a smaller molecular volume than the *exo* ones. This result is in agreement with the experimental data, in which the *endo* product of a Diels−Alder reaction is generally favored at high pressures.[23]

Conclusions

For the Diels−Alder reaction between 2-phenylcyclopentadiene and α-(methylthio)acrylonitrile, *ab initio* calculations show the existence of four transition structures on the potential energy surface corresponding to the formation of *para*/*endo*, *para*/*exo*, *meta*/*endo*, and *meta*/*exo* adducts. The four reactive channels correspond to asynchronous concerted mechanisms. The formation of the *para* adducts takes place with smaller energy barriers than the formation of the *meta* products. The presence of an electron-releasing substituent, a phenyl group, on the C2 carbon atom produces a more favorable stabilizing interaction in the *para* transition structures. The location of the sulfur atom in the dienophile system yields a favorable interaction between the lone pair on this atom and the π system of the diene fragment at the *endo* transition structures. The theoretical results can explain the experimental data, and the stereo- and regioselectivity are correctly predicted at all levels of calculation. Accurate enthalpies of activation have been obtained when the correlation energy is estimated at the MP3 level.

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