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A Density Functional Theory Study of Secondary Orbital Overlap in *Endo* Cycloaddition Reactions. An Example of a Diels−Alder Reaction between Butadiene and Cyclopropene

Branko S. Jursic

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

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Density functional theory (B3LYP, BLYP) and *ab initio* (HF, MP2, and QCISD(T)) methods support the hypothesis that transition state structures for the addition of cyclopropene to butadiene is stabilized through interactions between the hydrogen of cyclopropene and the π-bond of butadiene. This finding is supported by the computions of bond orders and charge separations and by the differences in frontier orbital energies. Because the interactions between the hydrogen of cyclopropene and the π-bond of butadiene is possible only in an *endo* transition state structure, it is conceivable that the formation of an *endo* cycloadduct should be dominant. This is confirmed by the computation of a lower activation barrier, ~2.0 kcal/mol, for the *endo* transition state structure than for the *exo* transition state structure.

Introduction

Wiberg reported the Diels−Alder reaction between butadiene and cyclopropene,[1] and Baldwin estimated from the reaction between cyclopropene and 1-deuteriobutadiene at 0 °C that 99.4% of the formed cycloadduct is the *endo* isomer.[2] There are many suggestions which attempt to explain *endo* selectivity in Diels−Alder reactions (Alder's rule[3]), but none are firmly established. According to Woodward and Hoffmann,[4] the preference is the result of favorable secondary orbital interactions (SOI) or secondary orbital overlap[5] between the diene and dienophile in the corresponding transition state structure. There are excellent figures and arguments for enhanced SOI in the *endo*-activated complex for cyclopropene with butadiene and cyclopentadiene, respectively.[5b,c] One can also find an explanation for the reaction preference in the difference between primary overlap,[6] volumes of activation,[7] and the polarity of the transition states.[8] Secondary orbital overlaps between a diene and a dienophile do not lead to bonds in the adduct, but primary orbital overlaps do.

There is no doubt that the driving force for cyclopropene as the dienophile for a Diels−Alder reaction is the release of angle strain energy in the course of the reaction. This is demonstrated by its relatively low activation barrier. For example, cyclopropene reacts with cyclopentadiene and butadiene at 0 °C or at room temperature, producing almost exclusively the *endo* cycloadduct.[1] Here we present a density functional theory (DFT) computational study of the butadiene cycloaddition reaction with cyclopropene.

Computational Methodology

All computational studies were performed with the Gaussian 94 computational package.[9] The Hartree−Fock (HF),[10] second-order Møller−Plesset (MP2)[11] perturbation, and quadratic configuration interactions [QCISD(T)][12] *ab initio* computational studies were the only *ab initio* computational methods employed. Two of the most popular DFT methods were used B3LYP and BLYP. The hybrid B3LYP is based on Becke's three-parameter functional,[13] which has the form $AE_x^{Slater} + (1 - A)E_x^{HF} + B\Delta E_x^{Becke} + E_c^{VWN} + C\Delta Ec^{nonlocal}$, where VWN is a correlation functional provided by the Vosko−Wilk−Nusair[14] expression and the nonlocal correlation is provided by the LYP[15] expression. The BLYP gradient-corrected DFT method combines Becke's 88 exchange functional[16] and Lee−Yang−Parr's correlation functional. Explanations for these DFT methods, basis sets, and *ab initio* methods can be obtained elsewhere.[17] Bond orders were calculated from natural bond population analyses using the Spartan computational package.[18]

Results and Discussion

The structures of the two isomeric transition state structures and their structural parameters are presented in Table 1. The most significant structural parameters which change with different theory levels are the bond distances. We have demonstrated, using different theory levels, that transition state structures in general do not

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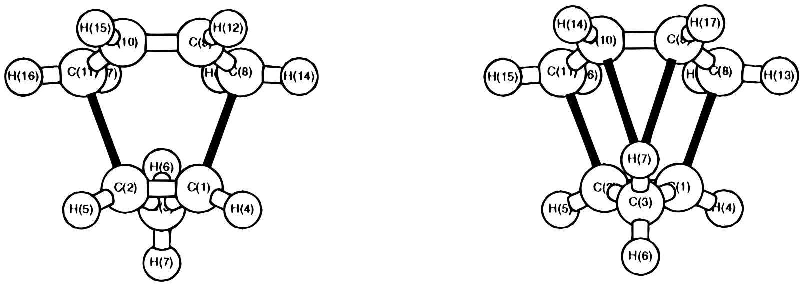
Table 1. Some Geometric Parameters for the *Exo* and *Endo* Transition State Structures



theory model	r_{81}/Å	r_{98}/Å	r_{109}/Å	r_{21}/Å	r_{36}/Å	a_{218}/deg	a_{321}/deg
			Exo Transition State Structure				
HF	2.260	1.366	1.407	1.336	1.489	110.0	63.4
B3LYP	2.378	1.370	1.423	1.338	1.500	109.6	63.5
BLYP	2.418	1.381	1.431	1.349	1.513	109.5	63.5
			Endo Transition State Structure				
HF	2.259	1.366	1.408	1.335	1.479	109.9	63.2
B3LYP	2.384	1.370	1.424	1.340	1.492	109.5	63.3
BLYP	2.424	1.383	1.433	1.351	1.505	109.4	63.3

Table 2. Total Energies (Hartrees) for the Reactants and the Transition State Structures and the Corresponding Reaction Barriers (kcal/mol) as Computed with *ab Initio* and DFT Methods Using the 6-31G(d) Basis Set[a]

theory	E_{I}	E_{II}	E_{exo}	E_{endo}	ΔE_{exo}	ΔE_{endo}	IF$_{exo}$	IF$_{endo}$
A	−115.823 048	−154.919 654	−270.684 852	−270.688 005	36.3	34.3		
B	−115.762 531	−154.828 117	−270.529 404	−270.532 483	38.4	36.5	−793.8	−770.5
C	−116.203 921	−155.421 123	−271.614 108	−271.618 828	6.8	3.9		
D	−116.068 973	−155.268 661	−271.312 496	−271.315 321	15.8	14.0		
E	−116.619 038	−155.992 144	−272.586 543	−272.589 706	15.4	13.5		
F	−116.562 769	−155.906 671	−272.442 052	−272.445 188	17.2	15.2	−437.1	−411.0
G	−116.556 554	−155.904 252	−272.438 448	−272.441 187	14.0	12.3		
H	−116.502 109	−155.821 268	−272.298 512	−272.301 116	15.6	14.0	−380.9	−360.1

[a] A = HF/6-31G(d); B = HF/6-31G(d) + zero point vibrational correction (ZPVC); C = MP2/6-31G(d)//HF/6-31G(d); D = QCISD(T)/D96V/HF/6-31G(d); E = B3LYP/6-31G(d); F = B3LYP/6-31G(d) + ZPVC; G = BLYP/6-31G(d); H = B3LYP/6-31G(d) + ZPEC; E_{I} = total energy for cyclopropene; E_{II} = total energy for 1,3-butadiene; E_{exo} = total energy for *exo* transition state structure; E_{endo} = total energy for *endo* transition state structure; ΔE_{exo} = activation barrier for the addition through *exo* transition state structure; ΔE_{endo} = activation barrier for the addition through *endo* transition state structure; IF$_{exo}$ = imaginary frequency for *exo* transition state structure; IF$_{endo}$ = imaginary frequency for *endo* transition state structure in cm^{-1}.

vary substantially when computed with different computational methods. However, there are some cases in which these differences are large between HF and MP2 computed geometries.[19] This is true when we utilize unusual dienes and dienophiles. Cyclopropene, due to its angle strain, is an unusual dienophile which should require an electron correlational computational method to correctly compute its transition state geometry. This is perfectly demonstrated in the bond distance of the bonds being formed. All applied computational methods predicted transition state structures for the concerted synchronous formation of both C−C bonds. As usual, HF *ab initio* method produced considerably shorter bond distances. For example, the C−C bond in formation computed by HF is more than 0.1 Å shorter than ones computed by both the B3LYP and BLYP DFT methods. On the other hand, BLYP is known to produce slightly longer bond distances, and in this way it resembles MPn *ab initio* methods.[20] The DFT computed newly forming C−C bond distances (r_{81}, Table 1) for the *endo* transition state structure are slightly longer than for the *exo* transition state structure. This indicates that the former structure is also closer to the reactants. Considering the Hammond postulate,[21] the transition state structure which is closer in geometry to the reactants will have a lower activation energy, and the product formed through an *endo* transition state structure should be dominant in a kinetic-controlled cycloaddition reaction. As pointed out earlier, Wiberg and Bartley observed only an *endo* cycloadduct for the butadiene reaction with cyclopropene.[1]

Certainly the most reliable way to estimate the reactivity, as well as the selectivity, of a cycloaddition reaction is to compute the reaction barriers for the two isomeric reactions. The total energies for the reactants and the two isomeric transition state structures are presented in Table 2. The two transition state structures have one imaginary frequency in which its motions connect the reactants and the products of the cycloaddition reaction. As in many cycloaddition reactions, HF *ab initio* method predicted very high activation barriers.[22] If 36.5 kcal/mol is the correct activation barrier for the cycloaddition reaction, then the reaction could not possibly be carried out experimentally. On the other hand, MP2/6-31G(d)

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Table 3. Computed Mullikan Bond Orders (BO), Atomic Charges (AC), and Frontier Orbital Energies Computed for the Two Isomeric Transition State Structures[a]

	BO_{1-8}	BO_{1-9}	BO_{7-9}	BO_{6-9}	AC_7	AC_6	HOMO	LUMO
				Exo Transition State Structures				
A	0.309 20	−0.002 17	0.001 49	0.002 87	0.186 655	0.200 425	−0.297 42	0.134 87
B	0.269 10	0.005 15	0.001 95	0.003 60	0.196 100	0.211 378	−0.219 29	−0.016 34
C	0.276 17	0.002 23	0.002 23	0.003 80	0.197 703	0.210 441	−0.183 11	−0.039 24
				Endo Transition State Structures				
A	0.315 35	−0.000 92	0.017 26	0.000 57	0.200 079	0.204 007	−0.302 23	0.140 25
B	0.269 06	0.004 03	0.023 52	0.000 94	0.209 894	0.213 882	−0.223 31	−0.012 21
C	0.275 74	0.004 79	0.024 46	0.001 02	0.210 919	0.212 839	−0.186 84	−0.035 56

[a] A = HF/6-31G(d); B = B3LYP/6-31G(d); C = BLYP/6-31G(d).

computed activation barriers which are too low (3.9 kcal/mol, Table 2). This would suggest that the reaction should actually be diffusion controlled. Based on the information from the experimental procedure, this is obviously not the case.[1] The QCISD(T) computed activation barrier is one which would be expected from the experimental results (~15.0 kcal/mol).

We have demonstrated that the B3LYP hybrid DFT method is highly reliable for computing activation barriers for cycloaddition reactions.[23] Here B3LYP/6-31G(d) with a zero point energy correction estimated the activation barrier for the *endo* cyclopropene addition to butadiene to be 15.2 kcal/mol (Table 2). This is 2 kcal/mol lower than the computed value for the *exo* cycloaddition reaction. The gradient-corrected DFT method, BLYP, computed activation barriers which are 1−2 kcal/mol lower than the B3LYP/6-31G(d)-computed values. Both *ab initio* and DFT computational methods correctly prefer the *endo* over the *exo* cycloaddition. These energy differences vary from 1.6 kcal/mol as computed with BLYP/6-31G(d) to 2.9 kcal/mol as computed with MP2/6-31G(d).

Almost all current explanations used to account for the preference of *endo* over *exo* cycloaddition can be applied here. For example, the volume of the *endo* transition state structure is obviously smaller than the corresponding *exo* transition state structure. However, it is important to focus on those interactions between the dienophile and diene which can stabilize the two isomeric transition state structures. We have selected a few parameters which demonstrate the favorable interactions between the reactants in the *endo* transition state structure (Table 3). To determine the interactions between reactants in the transition state structures, we have computed bond orders.[24] There is no substantial difference between the computed bond orders for the bonds involved in the formation (C1−C8; C2−C11) of the two isomeric transition state structures with hybrid or gradient-corrected DFT methods. However, there is a noticeable difference in the secondary orbital interactions (SOI) between C1 and C9 (C2 and C10) of the diene−dienophile π-bonds. If these interactions are of a dominate nature, the *exo* transition state structure would have the lower energy, which is not the case. Other nonbonding interactions are between the methylene hydrogen of the cyclopropene moiety with the π-orbitals of the butadiene moiety of the transition state structures. This interaction is only present in the *endo* transition state structure, and in fact, this secondary molecular orbital overlap is higher than the C1−C9 secondary molecular orbital overlap in the *exo* transition state structure. This properly suggests that the *endo* transition state structure should have a substantially lower energy than the *exo* transition state structure. The effect of the methylene hydrogen of cyclopropene overlapping with the π-bond of the butadiene moiety in the *endo* transition state structure affects the charge distribution on the hydrogen atom. In going from the *exo* transition state structure to the *endo* transition state structure, the increase of positive charge is substantially higher for H7, which interacts with π-molecular orbitals (Table 3). The frontier molecular orbitals[25] of the transition state structures also indicate that there are additional stabilization interactions which decrease the frontier orbital energies in the *endo* transition state structure and therefore make the *endo* transition state lower in energy.

Conclusion

All of the utilized *ab initio* (HF, MP2, and QCISD(T)) and DFT (B3LYP and BLYP) methods predicted that the *endo* transition state structure for the cyclopropene addition to 1,3-butadiene has a lower energy than the isomeric *exo* transition state structure. The estimated energy difference is approximately 2 kcal/mol. While the HF *ab initio* calculation overestimated and the MP2 *ab initio* calculation underestimated activation barriers, QCISD(T) produced the expected activation barriers. However, it is the B3LYP/6-31G(d) theory model that we trust the most. The computed activation barrier of 15.2 kcal/mol is consistent with experimental data.

The preference of the *endo* over the *exo* transition state structure can be explained with secondary orbital interactions between the butadiene and cyclopropene moieties which are present in the *endo* but not in the *exo* transition state structure. The most intense of these interactions are between the methylene hydrogen of cyclopropene and the π-orbital of 1,3-butadiene. The increased molecular orbital overlap is demonstrated through an increased bond order and charge transfer and by lowering frontier molecular orbital energies in the *endo* transition state structure.

Supporting Information Available: Output files for transition stage structure (24 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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