Electronic Factors Influencing the Activation Barrier of the Diels–Alder Reaction. An Ab Initio Study

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Ab initio molecular orbital theory has been applied to a study of the parent Diels–Alder reaction between ethylene and 1,3-butadiene. An activation energy of 25.4 kcal/mol and an enthalpy of 49.1 kcal/mol have been calculated at the MP4SDTQ/6-31G* level of approximation. A full set of vibrational frequencies, calculated by using analytical second derivatives, exhibited a single imaginary frequency for a transition structure with C_s symmetry consistent with a synchronous pathway. A PMO analysis of the HF/6-31G* orbital energies suggests that the activation energy may be largely attributed to closed-shell repulsions between the filled orbitals of the addends. Both two- and four-electron interactions were found to be destabilizing and hence contributed to the origin of the barrier.

Introduction

During the past decade the Diels–Alder reaction[1a] has experienced a resurgence of activity within the synthetic community that has been accompanied by renewed interest in the mechanism of this classic cycloaddition reaction.[1b] The overall mechanistic aspects of the reaction have recently been critically reviewed by Sustmann,[1c] while Hehre[2] has provided a thorough analysis of those factors influencing the regioselectivity of bond formation and Dewar[3] has reported a detailed presentation of theoretical arguments pertaining to the subtleties of concerted versus stepwise pathways. The mechanistic controversy concerning the mechanistic dichotomy between single or multistep reaction pathways has generally been divided along computational lines. Semiempirical calculations favor an asynchronous pathway[3] while ab initio calculations typically endorse a concerted synchronous pathway.[4] This dilemma arises in part because restricted Hartree–Fock (RHF) calculations involve only doubly occupied orbitals and may favor a closed-shell or synchronous mechanism while unrestricted Hartree–Fock (UHF) and semiempirical treatments tend to be biased toward diradical intermediates. The question of an adequate level of accuracy of ab initio basis sets employed has also been raised.[3] Houk has reported transition structures calculated with the STO-3G[4b] and 3-21G[4c] basis sets. A single imaginary frequency was found at both RHF levels and a synchronous transition state with C_s symmetry was predicted. This continuing mechanistic debate has been fueled by Dewar,[3] who points out that the STO-3G model is known to give poor estimates of molecular energies while those calculated by the 3-21G basis are still generally inferior to MINDO/3 energies. In contrast to MINDO/3, AM1 agrees[3b] with the ab initio calculations[4-7] and predicts the transition states for the prototype Diels–Alder (DA) reaction of butadiene and ethylene or 1,2-disubstituted cyano ethylenes to be synchronous or nearly so. However, since AM1 predicted that cyano substituents would retard the DA reaction with butadiene, in marked contrast to experiments, Dewar[3] concluded that this must be an artifact of the RHF procedure and that DA reactions, with the possible exception of the prototype, cannot be synchronous. The distinction between a mechanism involving a biradicaloid transition state in preference to a biradical intermediate was clearly drawn. A discrete long-lived biradical has been rigorously excluded by Houk[4c] on the basis of a simple but clever deuterium-labeling experiment. Another major advance that allows a distinction between closed-shell species and biradicals is the development of multiconfigurational SCF theory.[6a] The advantage of the MCSCF approach lies in its ability to treat both closed- and open-shell processes on an equal footing. In an earlier report[6b] Bernardi et al. reported MCSCF calculations on this DA reaction that also predicted a synchronous transition structure. More recently,[6c] they have examined both symmetrical and unsymmetrical transition structures and found a barrier at the 4-31G level of 32.0 kcal/mol in support of the synchronous pathway. In the present report we do not enter into this controversy although we do report that a C_s transition state does exist for the simplest DA reaction between butadiene and ethylene at the RHF/6-31G* level of theory. Our principal goal is to identify those electronic factors that most influence the activation barrier for this synchronous process by employing perturbational MO theory based upon orbital energies calculated at the highest level of theory that is now practical.

Results and Discussion

Molecular orbital calculations have been carried out with the HF/6-31G* basis set using the GAUSSIAN 86 program system[8a] utilizing gradient geometry optimization.[8b] A

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Table I. Activation Barriers for Stationary Points on the Butadiene–Ethylene Diels–Alder Surface

basis set//geometry	absolute energies, au	$\Delta E^{\ddagger\,a,b}$		E_a	$\Delta S^{\ddagger}$ (T)
HF/3-21G//3-21G	−231.60321	35.9[a]	(32.46)[b]		
HF/6-31G//6-31G*	−232.79942		(40.06)		
HF/6-31G*//6-31G*	−232.87961	45.04	(41.15)		−20.6 (600)
MP2/6-31G//6-31G*	−233.36059		(18.76)		
MP2/6-31G*//6-31G*	−233.67906	16.58	(12.98)		
MP3/6-31G//6-31G*	−233.39563		(25.98)		
MP3/6-31G*//6-31G*	−233.71709	26.86	(23.37)		
MP4SDQ/6-31G//6-31G*	−233.41061		(27.68)		
MP4SDQ/6-31G*//6-31G*	−233.72721	28.97	(25.53)		
MP4SDTQ/6-31G//6-31G*	−233.43369		(22.56)		
MP4SDTQ/6-31G*//6-31G*	−233.76602	21.86	(18.42)	25.4[c]	
experiment		25.1[d]		27.5[e] 32.8–34.3[f]	

[a] Calculated for 0 K. [b] kcal/mol, the barrier is relative to *trans*-1,3-butadiene. The barriers in parentheses are relative to *cis*-1,3-butadiene. [c] Includes net zero-point energies (+2.73) and corrections to internal energies (−0.34) and RT to 600 K (+1.2 kcal/mol). Vibrational frequencies are scaled by $\nu = 0.8929\ \nu_{calcd}$. [d] Estimated at 0 K from data in footnote *e* (see ref 4c for a discussion. [e] Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198. [f] Calculated from cyclohexene cycloreversion data and its experimental heat of reaction. Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878. Tsang, W. *J. Chem. Phys.* **1965**, *42*, 1805. Tardy, C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508.

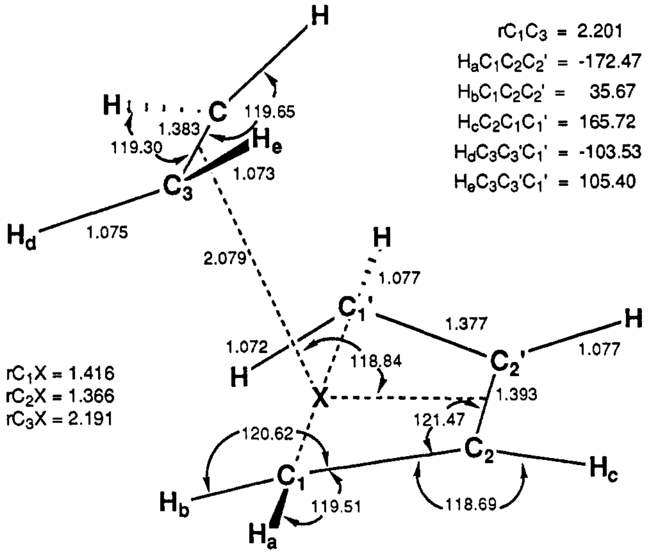
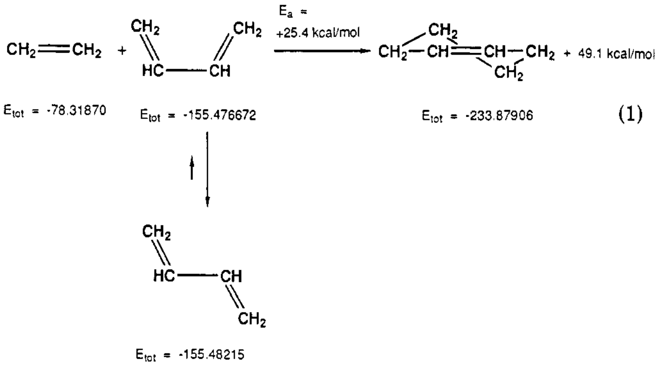


Figure 1. Optimized geometry (angstroms and degrees) of the transition state (6-31G*) for the Diels–Alder reaction of Butadiene with ethylene.

preliminary geomtry optimization utilized the HF/3-21G basis with C_s symmetry enforced. Relaxation of this constraint suggested that transition states of lower symmetry were higher in energy. More significantly, since our initial calculations Houk[4c] has shown this transition structure to exhibit a single imaginary frequency. A barrier of 32.5 kcal/mol, relative to *cis*-1,3-butadiene, was calculated.[9] With an extended basis including polarization functions, we find a significantly higher barrier of 41.1 kcal/mol at the Hartree–Fock level (RHF/6-31G*), Table I). However, a more realistic barrier in good agreement with experiment is found when an estimate of the correlation energy was included. As anticipated,[10] when all valence and virtual orbitals were included and electron correlation was calculated via Møller–Plesset perturbation theory to second order, the reduction in the barrier was greatly exaggerated (MP2/6-31G*, frozen core approximation). Much better results were obtained by a third-order treatment of the correlation. When both polarization functions and electron correlation to full fourth order (MP4SDTQ/6-31G*, frozen core) are taken into account, the best estimate of the activation energy, 25.4 kcal/mol, after zero-point energy and heat capacity corrections is remarkably close to the experimental value. The significant reduction in the barrier by including the triple excitations is also worthy of note. For comparison with experimental barriers the thermodynamically stable trans isomer of 1,3-butadiene was used (eq 1). This study clearly demonstrates that the correlation energy in such calculations is required in order to get accurate activation energies for Diels–Alder reactions and for pericyclic reactions in general.[11]



(1)

A full set of vibrational frequencies was calculated by using analytical second derivatives at the RHF/6-31G* level. Only one imaginary frequency was found, indicating that the C_s structure is a true transition state (Figure 1) and that all distortions to lower symmetry yield a higher barrier. These calculations are therefore in complete agreement with previous ab initio calculations that have predicted a synchronous pathway.[4-7] Our conclusions are based upon a higher level of theory and will hopefully remove one of the major criticisms[3] of prior predictions[4-7] based upon ab initio methods.

The thermodynamic properties associated with this DA reaction have also been a subject of controversy. The exothermicity (ΔH^0 = −49.08 kcal/mol, MP4SDTQ/6-

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(9) The total energy of this transition structure, −231.60321 au, was identical with that reported earlier by Houk.[4c] The reported barrier of 35.9 kcal/mol was relative to *trans*-1,3-butadiene. The barrier corrected for zero-point energy and heat capacity was 38.3 kcal/mol.

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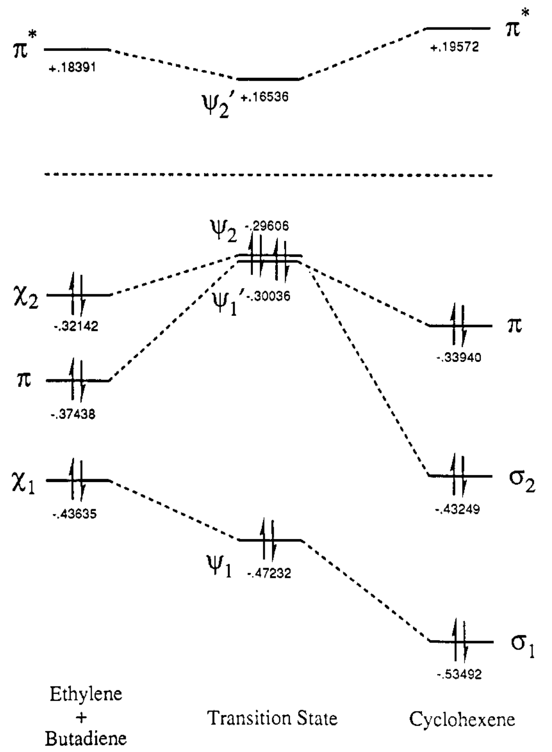

Figure 2. Frontier orbital energy changes (HF/6-31G*, au) for the synchronous Diels–Alder reaction affording cyclohexene.

31G*, eq 1) of the cycloaddition can easily be rationalized since the double bond of ethylene correlates with the more stable disubstituted π bond in cyclohexene and the conjugated π bonds of butadiene are transformed into two σ bonds in the product (Figure 2). All three occupied frontier orbitals of cyclohexene are lower in energy than those of the reactants. While an early transition state would be consistent with the Hammond postulate, the origin of the surprisingly high barrier remains an enigma. The role of closed-shell repulsion and orbital energy changes resulting from geometric distortion of the addends was first recognized by Salem in his insightful ab initio treatment of this fundamental cycloaddition reaction.[7] It has been suggested that a good part of the activation energy can be traced to the energy increase of the filled π orbital of ethylene.[7] The closed-shell repulsion energy or four-electron destabilization,[12] calculated in the traditional manner from frontier MO theory, has been estimated to be 4.4 kcal/mol.[4a]

We have previously emphasized the importance of closed-shell repulsion or HOMO–HOMO interactions for a variety of reactions.[10,13] In a symmetrical DA reaction the HOMO are of opposite symmetry and overlap is precluded. However, a significant closed-shell repulsion does exist between the HOMO of the dienophile (π) and the NHOMO of the diene (χ_1). The principal electronic interaction along the reaction pathway prior to the transition state involves only the six π electrons of the reactants since all other molecular orbitals are nearly orthogonal or overlap weakly. The mixing of the π orbitals is naturally divided into two subsets of three MO interactions by symmetry. A solution to the 3 × 3 secular equation[14] derived from the simultaneous interaction of χ_1, π, and χ_3 (Figure 3a) suggests that the four-electron destabilization[15] is 7.7 kcal/mol (3-21G). The accompanying 3 MO two-electron stabilization energy involving χ_2, π^*, and χ_4 (Figure 3b) is −20.7 kcal/mol.[14] Thus, on the basis of net energy change in the frontier orbitals[15] calculated from an extension of classical FMO theory, one would predict that the DA reaction should proceed without a significant barrier. This prediction stands in marked contrast to the energy changes given in Figure 3 that are based upon actual energy levels of the fully optimized reactants and transition state calculated by ab initio methods. We were therefore prompted to examine more closely the energetic consequences of these orbital interactions by high level ab initio methods.

Two of the opposing forces that contribute to the activation barrier are the extent of bond formation and the electronic repulsion between the two interacting fragments. The bond distance between the carbon atoms of the two developing carbon–carbon bonds at the transition state is 2.201 Å. A qualitative estimate of the bond order between the carbon atoms of the termini at the transition state may be obtained from the reduced Mulliken overlap population. By these criteria each developing C–C bond is only about 22% of that in cyclohexene (Figure 4). The net change in one-electron orbital energies for the interacting frontier orbitals shows that *both the four- and the two-electron interactions are repulsive* by 26.6 and 13.2 kcal/mol, respectively (Figure 3). Assuming an enthalpic contribution of approximately 36 kcal/mol due to C–C bond formation and a difference between the net increase in energy of 79.6 kcal/mol of the doubly occupied π orbitals at the transition state provides a reasonable estimate of the activation barrier (41.1 kcal/mol) prior to correction for electron correlation.

In addition to the exhaustive electronic reorganization required by this pericyclic process, geometrical distortion of the two addends also increases the total energy of the system. The π bonds in ethylene and *cis*-1,3-butadiene are elongated at the transition state by 0.066 and 0.055 Å, while the C_2–C_3 bond in the latter is contracted by 0.087 Å. The terminal hydrogens of ethylene and butadiene are bent out of plane by 13.4° and 13.8°, respectively. When the transition structure is dissected into the two geometrically distorted reactants, the increase in the total energy of the ethylene fragment at the MP4SDTQ/6-31G* level is 8.3 kcal/mol, while the energy required to distort butadiene to its transition-state geometry is 16.5 kcal/mol. Thus, the approximate "bond making" contribution (~36 kcal/mol) to the potential energy is substantially offset by the energy increase due to "bond breaking" (24.8 kcal/mol) and one is again left with the conclusion that the activation barrier for this archetype cycloaddition is largely due to closed-shell repulsion. These observations suggest that the transition structure, when described within the context of the Hammond postulate, provides a useful qualitative guide to the steric interactions along the reaction path. On the basis of the limited extent of C_1C_3 bond formation (about 22%) an early transition state would be indicated, while the degree of geometric distortion of the butadiene fragment is consistent with a late transition state. Thus extensive changes in both energy and geometry of the butadiene fragment suggest that considerations based upon the ground state may not be reliable.

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[15] The orbital energies of the ground-state reactants and those of the transition state after mixing were obtained from 3-21G calculations. The group overlap integrals S_{ij} and k from the Mulliken approximation were obtained from the ab initio matrix elements at the transition-state geometry.

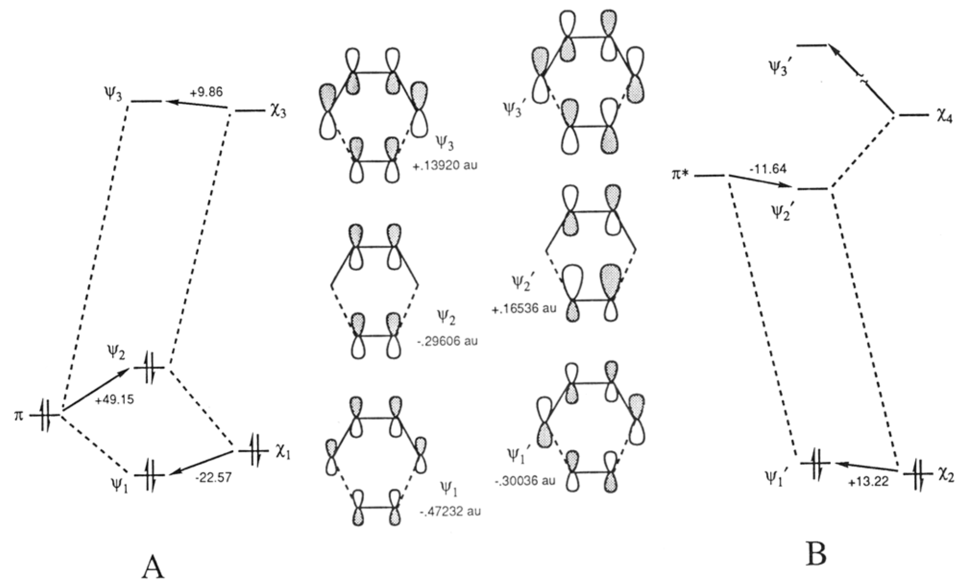


Figure 3. Extended FMO model showing the four-electron (A) and two-electron (B) interactions (kcal/mol) involved in the DA reaction (HF/6-31G*).

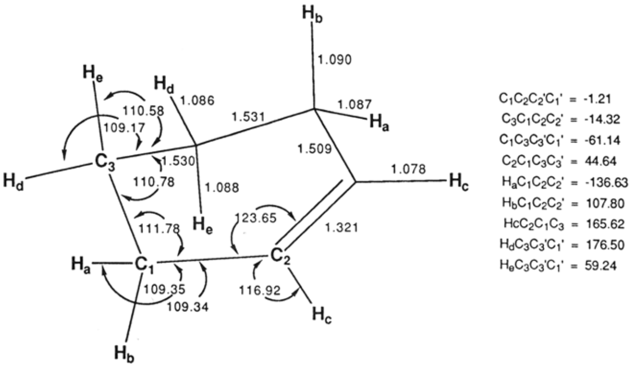
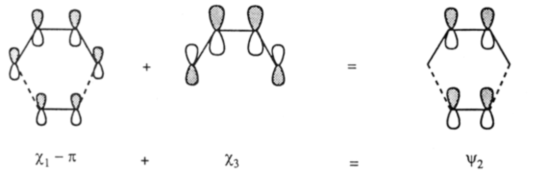


Figure 4. Optimized geometry (angstroms and degrees) of cyclohexene (6-31G*).

The synthetic chemist has in general found FMO theory very useful for predicting the regiochemistry of DA products. However in many instances the theory would fail and the wrong isomer would be predicted and no apparent reason was obvious. The success of a FMO analysis depends upon the validity of the assumption that the relative energies of the frontier MOs of the ground state will not be altered significantly on going to the transition state. Upon examination of the orbital energy changes attending the four-electron component (Figure 3a) the orbitals of like symmetry, χ_1 and π, do not cross (Figure 2) but experience an orbital splitting as anticipated by FMO theory. The lowest filled orbital is stabilized by 22.6 kcal/mol while the upper antibonding combination has increased in energy by 49.2 kcal/mol. The accompanying two-electron 3 MO interaction (Figure 3b), however, does not appear to comply with the basic tenets of FMO theory and one is immediately struck by the fact that χ_2 and π^* move in the opposite direction to that predicted. Thus, χ_2 and π^* experience an *orbital narrowing* and the bonding combination comprising these orbitals is *destabilizing* by 13.2 kcal/mol. However, the major portion of the increase in χ_2 is due to geometric distortion since the orbital energy of χ_2 in *cis*-1,3-butadiene, calculated at the transition state geometry, has increased by 17.4 kcal/mol. This MO is probably lowered slightly in energy by its interaction with π^* as anticipated. The lengthening of the double bonds of the diene is also responsible for the decrease in the energy of χ_3. Thus, it is obvious that frontier HOMO–LUMO interactions dominate neither the incipient stages of the reaction nor the energies of the transition state. This EFMO analysis suggests that the observed barrier may be largely attributed to the increase in one-electron orbital energies of 39.8 kcal/mol resulting from *both* symmetry allowed interactions. The overall barrier, however, must reflect the enthalpic balance between bond-breaking or angle deformation and bond-making, as well as closed-shell repulsion. It is also evident that qualitative FMO theory fails badly in this instance since large geometric perturbations occur on going from the ground state to the transition state that result in significant destabilization of a key frontier orbital. As noted above, EFMO theory[14] predicts a two-electron stabilization of Ψ_1' (−20.7 kcal/mol) while the more quantitative estimate based upon ab initio calculations suggests an energy increase of 13.2 kcal/mol (Figure 3b).

The above extended FMO analysis of the energetics of the π orbitals,[14] however, does have far reaching consequences concerning the regiochemistry of the DA reaction. Within the context of the three molecular orbital, four-electron model,[10] the lower orbitals (Ψ_1 and Ψ_1', Figure 3) will be bonding, and the highest unoccupied orbitals (Ψ_3 and Ψ_3') antibonding throughout the reaction pathway. When a symmetrical transition state is involved, mandatory mixing between orbitals of opposite sign results in complete atomic orbital coefficient cancellation at the interacting termini of the central orbital within each subset (Figure 3). This is a general phenomenon that occurs in substitution, elimination, and pericyclic reactions.[10,13] Both of the developing central orbitals (Ψ_2 and Ψ_2') on the reaction pathway prior to the transition state are largely comprised of an upper antibonding combination as depicted in Figure 3. Before bonding can be achieved in both occupied σ orbitals of cyclohexene, a change in phase at the termini (C_1–C_3) must be achieved. Mixing of the developing central orbitals Ψ_2 and Ψ_2' with virtual orbitals χ_3 and χ_4 as described in eq 2 and 3 affords MOs with nonbonding interactions between the termini at the transition state. *After the barrier is crossed*, a bonding interaction between C_1 and C_3 will develop as χ_1 is transferred into σ_1 and χ_2 into σ_2 of cyclohexene (Figure 2). When substituents are involved, the transition state has lower symmetry and an exact cancellation of the coefficients at the terminal carbons of the transition structure



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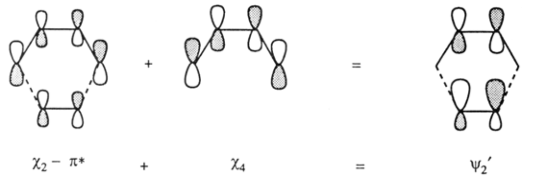

(3)

will not occur, but a change in phase from antibonding to bonding at some point near the transition state must still be realized in Ψ_2 and Ψ_2' in order to consummate σ bond formation in the product. When substituents are present in the diene or dienophile, the coefficients at C_1 and C_4 will therefore be greatly reduced in magnitude due to phase cancellation involving atomic orbitals of opposite sign and different size coefficients. Consequently, neither Ψ_2 nor Ψ_2' (Figure 3) contain significant regiochemical information. Regiochemical predictions of the normal DA reaction based upon classical FMO theory are normally predicted upon the assumption that the preferred two-electron HOMO–LUMO interaction (Figure 3b) is stabilizing and will exert the greatest influence upon the stereochemistry of the reaction. This prediction, based upon ground-state arguments, is obviously not translated to the transition state (Figure 3b) and is most likely responsible for many of the shortcomings of FMO treatments of the DA reaction.[2] Indeed, the only molecular orbital in either subset that is lowered in energy is Ψ_1 (Figure 3a) resulting from the four-electron interaction that has typically been ignored in such theoretical studies. Inclusion of the atomic coefficients of this lower lying orbital in an FMO analysis of the regiochemistry of the DA reactions does increase the predictability of the preferred orientation of the reactants.[14]

Finally, we address the question of aromaticity in the transition state for the DA reaction. Although it may be convenient to describe this pericyclic reaction as being aromatic in an orbital symmetry sense, there is no reason to assume a priori that "aromatic character" of the transition state will significantly lower the activation barrier. For example, the paragon reaction forming benzene via the trimerization of acetylene enjoys no aromatic stabilization at the transition state since aromaticity is realized after the barrier is crossed despite the planarity of the transition structure.[10] In the DA reaction a nonplanar "boat-like" geometry is involved in a reaction where two π bonds are converted to two σ bonds in the product. Because of the developing σ bonds, such a transition state could at best be considered homoaromatic in nature. Therefore, any contribution to the barrier from aromatic stabilization must necessarily occur prior to the transition state. No such stabilization is in evidence upon examination of the orbital energies in Figure 3. The consequence of distortion of the conjugated periphery of aromatic systems has recently been discussed.[17]

We therefore conclude that the highest level of theory reasonably possible at this time clearly predicts that a concerted transition state for the simplest of DA reactions is synchronous and not distorted to lower symmetry and that the surprisingly high activation barrier is largely due to closed-shell repulsion between filled π orbitals. We have identified the "culprit orbital" that contributes most significantly to the barrier as Ψ_2, the *nonbonding* HOMO arising from the compulsory mixing of π and χ_1. It is also noteworthy that Ψ_1' involving the so-called "two-electron stabilizing" component also contributes to the activation barrier. At the transition state Ψ_2 is only slightly higher in energy (2.7 kcal/mol, Figure 2) than the orbital (Ψ_1') resulting from the celebrated "stabilizing" HOMO–LUMO interaction between χ_2 and π^*. Thus, a simple HOMO–LUMO treatment is not adequate to explain either the regiochemistry or the energetics of the DA reaction. When all three orbitals within each symmetry compatible subset are explicitly treated at the ab initio level, reactivity trends are much better understood and some additional information concerning stereochemistry becomes available.

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Registry No. Ethylene, 74-85-1; 1,3-butadiene, 106-99-0.

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