A Theoretical Study of the Endo/Exo Selectivity of the Diels−Alder Reaction between Cyclopropene and Butadiene

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Abstract: Molecular orbital calculations using Hartree−Fock (HF), complete active space self consistent field (CASSCF), quadratic configuration interaction with single and double excitations, and triple excitations included via perturbation (QCISD(T)) and semiempirical (AM1) methods suggest that the experimentally observed endo selectivity for the Diels−Alder reaction between cyclopropene, **I**, and isotopically substituted butadiene, **II**, be mostly due to an attractive interaction between a C−H of **I** and the π-bond between the central carbons of **II**, which is possible in the endo (but not exo) transition state. The relevance of this observation to other Diels−Alder endo/exo selectivities is discussed. The activation energetics for the reactions are all substantially overestimated by HF and CASSCF calculations, while QCISD(T) and AM1 give more reasonable results. Only AM1, however, fails to predict the observed preference for the endo TS. Both QCISD(T) and small basis set calculations are shown to result in large basis set superposition errors, which fortuitously lower the (uncorrected) activation energies.

The Diels−Alder reaction has been extensively studied by both experimental and theoretical methods. A preference for formation of endo product is usually (but not always) observed. Although several reasonable suggestions have been proposed to explain the observed selectivity, none is firmly established. One of the more popular explanations attributes the endo preference to secondary π-orbital overlap[1] in the transition states. Other explanations invoke differences in primary overlap,[2] the differential volumes of activation,[3,4] and different polarities of the transition states.[5]

Wiberg reported the Diels−Alder reaction of cyclopropene, **I**, with butadiene, **II**, in 1960.[6] Baldwin has recently reported that **I** and 1(E)-dideuteriobutadiene, **IIa**, form Diels−Alder product with complete (within the reported limits of detection) endo selectivity at 0 °C.[7] The nature of the reagents excludes secondary π-orbital overlap as defined by Gleiter.[1] Furthermore, it is difficult to understand how polarity of the transition states or the differential volumes of activation can explain the

experimental observation. Despite the above, a recent communication suggests that secondary orbital overlap is the determining factor in the selectivity.[8]
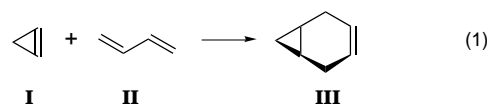
A report of small basis set (6-31G/3-21G) ab initio calculations[9] gives a difference in activation energies consistent with the quantitative experimental result. However, we show below that this fortuitous result derives from failure to consider the effect of basis set superposition error (BSSE).

Many groups have studied Diels−Alder reactions using different MO techniques. Controversy abounds on the degree of asynchronicity extant in the transition states for even the simplest cases. For example, the prototype reaction of butadiene with ethylene has been reported to be variously synchronous,[10] to be asynchronous,[11] and to have two competitive reaction paths with the synchronous path slightly favored.[12] Biradical mechanisms have also been proposed.[13] Experiments show that other clearly unsymmetrical Diels−Alder reactions can proceed via biradical reaction paths.[14]

In this paper, we examine the possible transition states for the reaction of cyclopropene with butadiene using several molecular orbital (MO) methods, including Hartree−Fock (HF), CASSCF, and semiempirical (AM1) procedures. Our goal is to understand the endo/exo selectivity. We shall specifically discuss the possible contributions of a C−H···π hydrogen bond in the transition state and secondary orbital overlap.

Methods

We performed MO calculations at various levels using several programs. HF calculations with the 6-31G, 6-31G*, 6-31G**, D95, and D95* basis sets were performed using GAUSSIAN 92 and 94

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(15) Gaussian, Inc., Pittsburgh, PA.

Table 1. Energetics of Diels−Alder Reactions[a]

		HF			CAS		QCISD(T)	
		3-21G	D95	D95*	D95V	D95V*	D95V	D95V*
s-cis biradical					−270.712844			−271.724692
s-trans biradical					−270.719587			−271.732231
TS endo	energy	−269.181366	−270.600062	−270.718320	−270.690856	−270.804995	−271.315321	−271.720205
	ZPVE	98.01	97.80	97.12				
	CP	9.02	1.63	1.10	1.26	1.10	8.49	6.82
TS exo	energy	−269.177287	−270.596808	−270.715185	−270.688714	−270.802925	−271.312496	−271.716958
	ZPVE	97.95	97.71	97.06				
	CP	8.45	1.59	1.07	1.24	1.07	8.33	6.72
ΔE		−75.08	−70.82	−69.54				
	corr	−68.50	−63.65	−62.29				
ΔE_{act} endo		25.16	32.90	35.82	33.38	33.82	14.57	12.68
	corr	36.33	36.60	39.00	36.51	36.79	24.91	21.37
ΔE_{act} exo		27.72	34.95	37.78	34.72	35.12	16.34	14.71
	corr	38.26	38.52	40.88	37.74	38.01	26.45	23.25
$\Delta\Delta E_{act}$		2.56	2.04	1.97	1.34	1.30	1.77	2.04
	corr	1.93	1.92	1.88	1.24	1.22	1.54	1.88

[a] Energies in hartrees for ab initio total energies, otherwise in kcal/mol. Corrected values (cor) include CP and ZPVE corrections. [b] Values are for ΔH at 298 K.

programs.[15] Unrestricted Hartree−Fock (UHF) calculations were attempted for several transition states. They all converged to the RHF result.

AM1 calculations were performed using AMPAC 2.1[16] and 4.5[17] programs. The concerted transition states were calculated by using the RHF procedure, while the biradical reaction paths were calculated by using the "BIRADICAL" keyword which does 3 × 3 CI starting from an open shell SCF wave function. Optimization using 2 × 2 CI with the RHF wave function would not converge.

CASSCF calculations were performed using Sirius[18] and Abacus[19] programs with an active space consisting of six electrons in the six π-orbitals of the reagents and the corresponding orbitals of the transition state. Both D95 and D95V* basis sets were used.

The biradical intermediates were optimized using CASSCF option in the GAMESS[20] program with the D95V basis set and the same active space used for the transition state.

Single point quadratic CI calculations with singles and doubles including perturbative estimations of triple excitations, QCISD(T),[21] were performed on each of the CASSCF optimized structures.

Correction for BSSE was performed using somewhat controversial[22] counterpoise (CP) method of Boys and Bernardi,[23] taking into account the distortion of the reagents as described elsewhere.[24]

We enforced a plane of symmetry that bisects the central bond of butadiene and the π-bond of cyclopropene for the CASSCF calculations on the concerted transition states. All geometrical optimizations were unconstrained using other procedures.

The PCMODEL[25] and MOLDEN[26] programs were used for generation of input (aided by preoptimization using MMX molecular mechanics force field[27]) and graphics.

(16) Graciously furnished by Eamonn Healy and M. J. S. Dewar.

(17) SemiChem, Shawnee, KS.

(18) Sirius is an MCSCF program by Jensen, H. J., Ågren, H., and Olsen, J.

(19) ABACUS is an MCSCF energy derivatives program by Helgaker, T., Jensen, H. J., Jørensen, P., Olsen, J., and Taylor, P. R.

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Table 2. Geometrical Parameters in Å

	HF		CASSCF		
	3-21G	D95	D95*	D95	D95*
cyclopropane					
C=C	1.2816	1.2969	1.2824	1.3172	1.3010
C−C	1.5232	1.5296	1.5027	1.5295	1.5045
C−H	1.0749	1.0772	1.0835	1.0765	1.0818
=C−H	1.0583	1.0622	1.0709	1.0620	1.0697
butadiene					
C=C	1.3203	1.3369	1.3289	1.3578	1.3499
C−C	1.4668	1.4719	1.4719	1.4710	1.4699
TS endo					
$C_a−C_b$	2.2813	2.2867	2.2617	2.3027	2.2926
$C_b−C_c$	1.3568	1.3775	1.3719	1.3972	1.3906
$C_c−C_c$	1.4121	1.4173	1.4128	1.4203	1.4170
$C_a−C_a$	1.3332	1.3551	1.3419	1.3816	1.3647
H−π	2.3349	2.4951	2.2980	2.5953	2.5997
C−H (π)	1.0805	1.0819	1.0875	1.0782	1.0829
C−H	1.0760	1.0776	1.0829	1.0769	1.0812
TS exo					
$C_a−C_b$	2.2773	2.2856	2.2642	2.3013	2.2937
$C_b−C_c$	1.3571	1.3773	1.3715	1.3976	1.3907
$C_c−C_c$	1.4101	1.4161	1.4123	1.4194	1.4165
$C_a−C_a$	1.3299	1.3521	1.3394	1.3802	1.3638
C−Ha	1.0789	1.0787	1.0859	1.0775	1.0821
C−Hb	1.0772	1.0807	1.0844	1.0777	1.0820

Results

The energetics of the forward and reverse Diels−Alder reactions of cyclopropene and butadiene proceeding via endo, exo and biradical reaction paths are summarized in Table 1.[28] A selection[29] of the corresponding geometric parameters are presented in Table 2 (also, see Figures 1−3). Since CASSCF does not generally provide a balanced treatment of electron correlation, one might expect inconsistencies in the energetics of the normal Diels Alder reaction. This point is illustrated by a recent report by Houk, where CASSCF calculations overestimated the stabilities of the reagents compared to the products and transition states for the Diels−Alder reaction between butadiene and ethylene.[30] Had the retro-Diels−Alder activation

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(28) A more complete table appears in the Supporting Information.

(29) Complete geometries for the endo and exo transition states are included in Supporting Information.

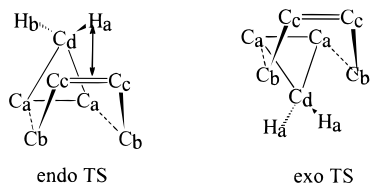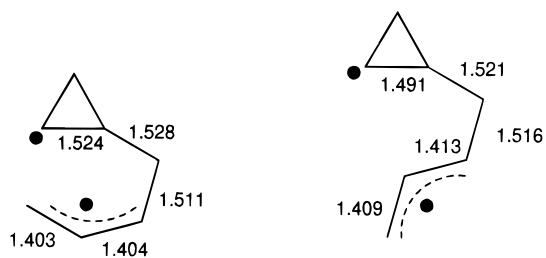(30) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478.

Figure 1. Endo and exo transition states.

Figure 2. Biradicals with optimized bond lengths (CASSCF/D95V*) indicated.

energies been compared (rather than the normal reaction), the activation energies of the CASSCF calculations would have been much closer to the experimental value. The QCISD method has been designed to be size-consistent. Although no experimental activation energy has been reported, the single-point QCISD(T) results give activations energies that are quite reasonable for a fast reaction at 0 °C. In the following discussion, we shall refer to the corrected QCISD(T)/D95V*//CASSCF/D95V* energies and geometries unless otherwise noted.

The activation energies for the concerted cycloaddition calculated by using several MO procedures are reported in Table 1. Hartree−Fock calculations have been performed using the 3-21G, D95, and D95* basis sets. Since the activation energies involve the energy difference between the TS and the separated reagents, we applied the CP and ZPVE corrections. The ZPVE correction is generally used for Diels−Alder calculations; however, the CP correction is often overlooked. While the HF activation energies vary considerably before correction (11-kcal/mol range), they are much more consistent after correction (3-kcal/mol range). The 3-21G basis set (included for comparison with Apeloig's report) has a particularly large CP correction. The CASSCF activation energies are similar to the better SCF values. The QCISD(T) values are significantly lower, more consistent with experiment.[7] ZPVE corrections to the CASSCF and QCISD(T) calculations were assumed to be 90% of the corresponding HF/D95 and HF/D95* values. The CP corrections calculated for the CASSCF/D95 calculations are similar to those for the HF calculations. However, the CP's for the QCISD(T) TS's are much larger than those for any of the other calculations except for those using the minimal 3-21G basis set. Other reports of QCISD(T) Diels−Alder TS's have not made this correction. The reported activation energies reported in them should be treated with caution.

The differences in the activations for endo and exo paths are consistently less than 2 kcal/mol for the corrected energies. Surprisingly, the HF calculations give the same selectivities as the best QCISD(T) calculation, despite the differences in calculated activation energies. AM1 gives activation enthalpies

(31) Single point AM1 with 3 × 3 CI with the closed shell SCF wave function (CI = 2 in AMPAC) lowers the activations energies by about 1 kcal/mol without changing the endo/exo selectivities. Optimization with this option did not converge.
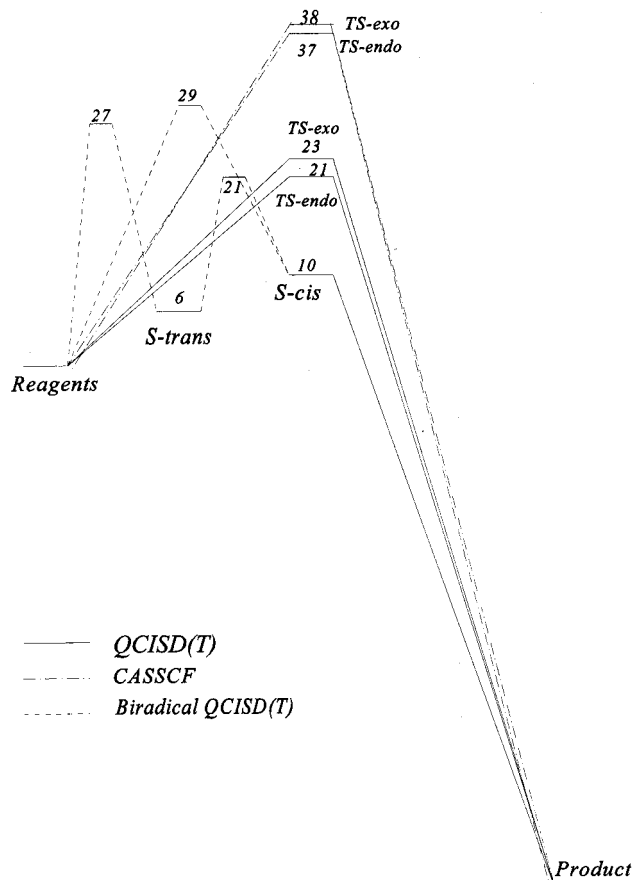

Figure 3. Energetics of various possible reaction paths. See text for an explanation of biradical QCISD(T) transition state energies.

very similar to the corrected QCISD(T)/D95V* activations,[31] but is the only method to favor the exo path (by 0.7 kcal/mol).[32] All ab initio calculations favor the endo reaction path. However, after corrections are applied, they all underestimate the endo preference of the experiment.

The experimental gas-phase enthalpy of reaction was calculated by using values for cylopropene and butadiene taken from Cox and Pilcher.[33] The enthalpy of bicyclo[4.1.0]cycloheptene was calculated by applying the heat of dehydrogenation of cyclohexene to the enthalpy of formation of bicyclo[4.1.0]-heptane using values from the same reference.[34] The HF/D95 and HF/D95* calculations accurately reproduced the experimental value determined by this method, while the magnitude of predicted enthalpy of reaction for HF/3-21G is greater and that for AM1 substantially greater.

Cyclopropene is a very reactive dienophile. This is probably due to the substantial decrease in angle strain energy upon formation of the adduct. Since a considerable amount of strain might be relieved upon formation of only one of the two new bonds, a biradical mechanism intermediate could be a possibility. Several Diels−Alder reactions are thought to proceed by such mechanisms.[35] In order to test this possibility, we calculated various biradical species (Table 1). We optimized the biradicals using the CASSCF/D95V method, then performed single-point QCISD(T)/D95V* calculations on these geometries. These

(32) The details of the AM1 results appear in the expanded tables of the Supporting Information.

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(34) Details appear in the expanded tables of the Supporting Information.

(35) For example, see: Ortí, J.; Branchadell, V.; Ortuño, R. M.; Oliva, A.; Font, J.; Bertràn, J.; Dannenberg, J. J. *J. Mol. Struct. (Theochem)* **1993**, *284*, 37.

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calculations are directly comparable to the QCISD(T) results for the concerted pathway. At this level, the s-trans and s-cis biradicals are 5 and 10 kcal/mol, respectively, higher than the reagents. The geometries are presented in Figure 2 and the energetics in Table 1 and Figure 3.

We did not locate the transition state for the formation of this species as the GAMESS program does not provide the efficient geometry optimization procedures necessary to render the calculation feasible with the computational resources available. However, we can estimate the activation energies using the relationship between the BDE of the bond formed or broken and the intrinsic barrier of a C−C bond that we have previously proposed.[36] This relationship predicts barriers of about 27 (s-trans) and 29 (s-cis) kcal/mol, which are significantly greater than the activation for either concerted pathway. The favored s-trans biradical must isomerize about the central bond of the butadiene to become capable of forming the adduct, a process which requires about 15 kcal/mol of activation energy. We can, therefore, rule out the biradical mechanism on the basis of our calculations, as well as the experimental observation of almost 100% endo selectivity.

Discussion

A possible explanation of the preference for the endo transition state might be a stabilizing interaction between one of the H's on C_3 of **I** interacting with the incipient C_2−C_3 double bond of **II** in the endo (but not exo) transition state. Such an interaction would be similar to that observed in some crystals[37] and in H_2O/acetylene[38] complexes. This explanation would be consistent with Apeloig's observation that C_3-substituted cyclopropenes give exo adducts with substituted butadienes, but other substituted cyclopropenes with H's at C_3 yield endo adducts.[39] Examination of the geometries of the endo and exo TS's supports this hypothesis. In particular, the two C−H bonds on the methylene carbon differ in bond length by a greater amount in the endo TS. The C−H pointing to the central π-bond of the butadiene moiety (C−H_a) is the longer of the two methylene C−H bonds in the endo TS (see Table 2). This observation suggests that the interaction between the C−H and π-bond is attractive. A repulsive interaction should shorten the C−H bond.

To further test this hypothesis, we calculated the C−H···π-bond interaction between two molecules of acetylene arranged in a T-shape.[40] Our results are consistent with the crystal stuctures and single point ab initio calculations recently reported.[31] The results indicate that the calculated stabilizing interaction varies little (from 0.8 to 0.9 kcal/mol) upon improving the level of calculation from HF/D95 to MP2/D95**. However, the H···π distance decreases substantially (from about 3.0 to 2.6 Å) upon application of MP2. The D95 and D95* Diels−Alder transition states probably provide a reasonable estimate of the energetic importance of this interaction, but may err in the H···π distance. Since the C−H···π-bond interaction in the Diels−Alder transition state is an intramolecular interac-
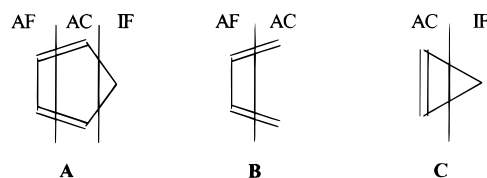

Figure 4. Examples of active centers (AC), active frames (AF), and inactive frames (IF) according to the definitions given by Gleiter[1] for cyclopentadiene (A), cyclopropene (B), and butadiene (C).

tion (the incipient C−C bonds already have brought the two separate reagent molecules together), there should not be a major vibrational correction to this interaction.

After most of the work described had been completed, Apeloig[8] suggested that secondary orbital interactions be the determining factor in the exo/endo selectivity (despite other recent reports that suggest that secondary orbital interactions are not determinant in similar cases).[41] The question is whether C−H···π H-bonding and secondary orbital interactions as discussed by Apeloig are physically different effects, as the terms "secondary orbital effect" (SOE), "secondary orbital interaction" (SOI), and "secondary interaction" (SI) have often been confused in the literature. The suggestion that secondary orbital overlap could be used to explain the endo selectivity of many Diels−Alder reactions is generally attributed to Hoffmann and Woodward.[42] The concept is based upon frontier molecular orbital (FMO) theory. The primary HOMO/LUMO interaction between the carbons at the bond-forming centers is augmented by a secondary interaction between other π-centers on the same pair of orbitals. Due to the spatial arrangements, this is generally only possible in the endo form of the transition state. Gleiter[1] has carefully defined the FMO possible interactions between diene and dienophile. He defined (see Figure 4) the first order orbital interactions as those between the active centers (AC), or the atoms forming the new bonds. He divided the second order orbital interactions into three parts. For this he divided the rest of the reagents into two zones. He called the "active frame" (AF) those atoms that are involved in σ/π reorganization but are not AC's. The inactive frame (IF) is defined as the molecular fragments not involved in the reaction. For example, he classified the 1- and 4-π-centers of cyclopentadiene (Figure 5A) as AC and the 2- and 3- π-centers as AF, while the CH_2 was classified as IF. Of three possible second-order interactions, secondary orbital effects was defined as interactions between the AF's of the two reagents. Interactions between the AF of one and the IF of the other are defined as "polar group effects". By analogy to cyclopentadiene, the CH_2 of cyclopropene would be considered to be the IF (Figure 5C). Thus, the FMO interaction between the CH_2 of the cyclopropene and central carbons of the butadiene (Figure 5B) would *not* be an SOE according to this definition.

Sustmann and Binsch have considered a complete perturbation[43] approach to Diels−Alder reactions. In their specific application to the reaction between cyclopentadiene and cyclopropene,[44] they found an attraction between a C−H bond on the cyclopropene to the central carbons of the cyclopentadiene π-system in the endo arrangement (as well as a repulsion between the CH_2's of the two reagents in the exo configuration). They referred to this as a secondary interaction. However, it differs substantially from the SOE or SOI's taken from FMO theory because the complete perturbation treatment (like the

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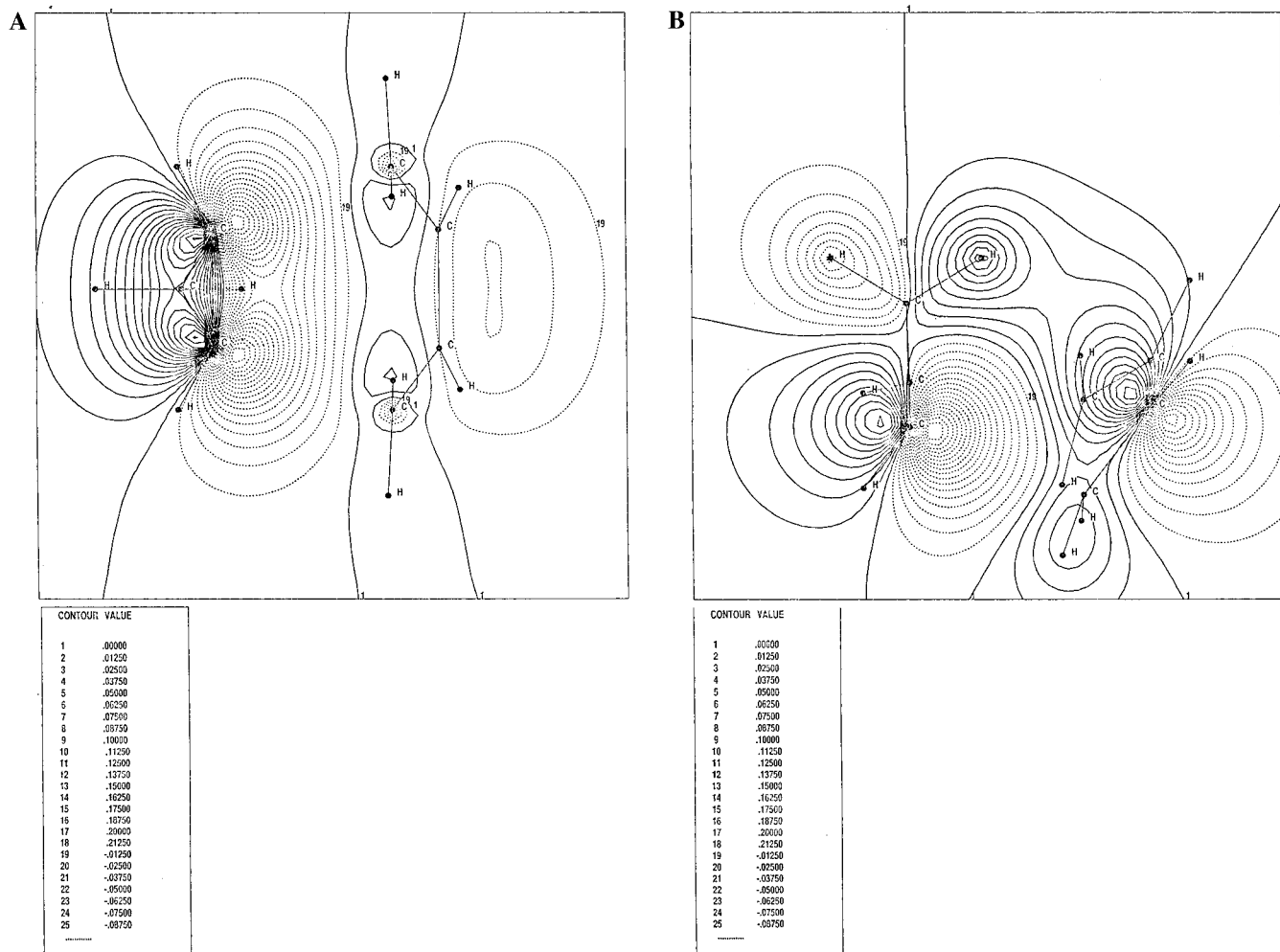(44) Sustmann, R.; Binsch, G. *Mol. Phys.* **1971**, *20*, 9.

Figure 5. Contour diagram of HOMO (orbital 26) (A) in the plane of the active four centers and (B) in the 2-fold symmetry plane that contains the cyclopropene CH$_2$.

variational MO treatment) considers interactions between all pairs of orbitals, not only the FMO's. In fact, Sustmann and Binsch found the attractive interaction between the C−H and π-orbitals to be greater than the primary interaction at large separation. To properly understand this, one must consider that the most stabilizing interaction will lead to a complex, or minimum on the energy surface. The FMO interaction is meant to define the path to a transition state, which is repulsive at long distance. If the secondary, C−H···π interaction that would stabilize a complex is operative for only one (i.e., endo) of two possible transition states, it would lower its energy. However, this is not necessarily an FMO effect, and therefore it is not properly defined as SOE or SOI in the sense normally used. Rather, it is another possible way to describe a C−H···π hydrogen bond.

Which kind of interaction determines the selectivity for the reaction at hand? Apeloig points out that symmetry restricts the FMO interaction to that between the HOMO of the cyclopropene and the LUMO of butadiene. To the extent that this interaction be dominant, one would expect some charge-transfer from the HOMO to the LUMO, or from the C−H to the C=C. In the calculations on the C−H···π interactions of the two acetylenes, we observed a small amount of charge transfer from the π-system to the C−H, or from the acceptor to the H donor.

The individual MOs (Figures 5 and 6, and Supporting Information) of the TS do not necessarily correspond to what may be expected from FMO theory. Furthermore, stabilization

of the HOMO of the TS may not be the dominant factor for the determination of the relative energetics of the endo and exo TS's. The HOMO for the endo TS is of A′ symmetry (see Figure 6). It can be thought of as the antibonding combination of the cyclopropene π-orbital and a π-orbital mostly on the 2- and 3−positions of butadiene. It is slightly antibonding between the active centers, but bonding for the C−H···π interaction. The HOMO-3 is the A′ MO that is bonding between the active centers (see Figure 7). It, however, is antibonding for the C−H···π interaction. The two intervening orbitals (HOMO-1 and HOMO-2) are of A″ symmetry, with no density on the C−H. HOMO-8 is bonding both at the primary centers and for the C−H···π interaction.

As the sum of the orbital energies counts the electronic (but not the nuclear) repulsions twice, the orbital energies are not going to necessarily reflect the cause of the endo/exo selectivities. Clearly, the electronic repulsions must be lower for the exo TS, so the endo orbital energies must be lower to compensate. Thus, the fact that the HOMO, HOMO-3, and HOMO-8 are all lower for the endo may not be significant.

We investigated the possibility that a deuterium kinetic isotope (KIE) effect might allow us to experimentally establish the C−H···π interaction in the transition state. Calculation of the differences in the activation energies (including ZPVE) for the transition states where either Ha or Hb is replaced by D indicated a difference of only 0.01 kcal/mol (CASSCF/D95). Thus, no measurable KIE would be predicted. One might expect an attractive C−H···π interaction to lower the stretching
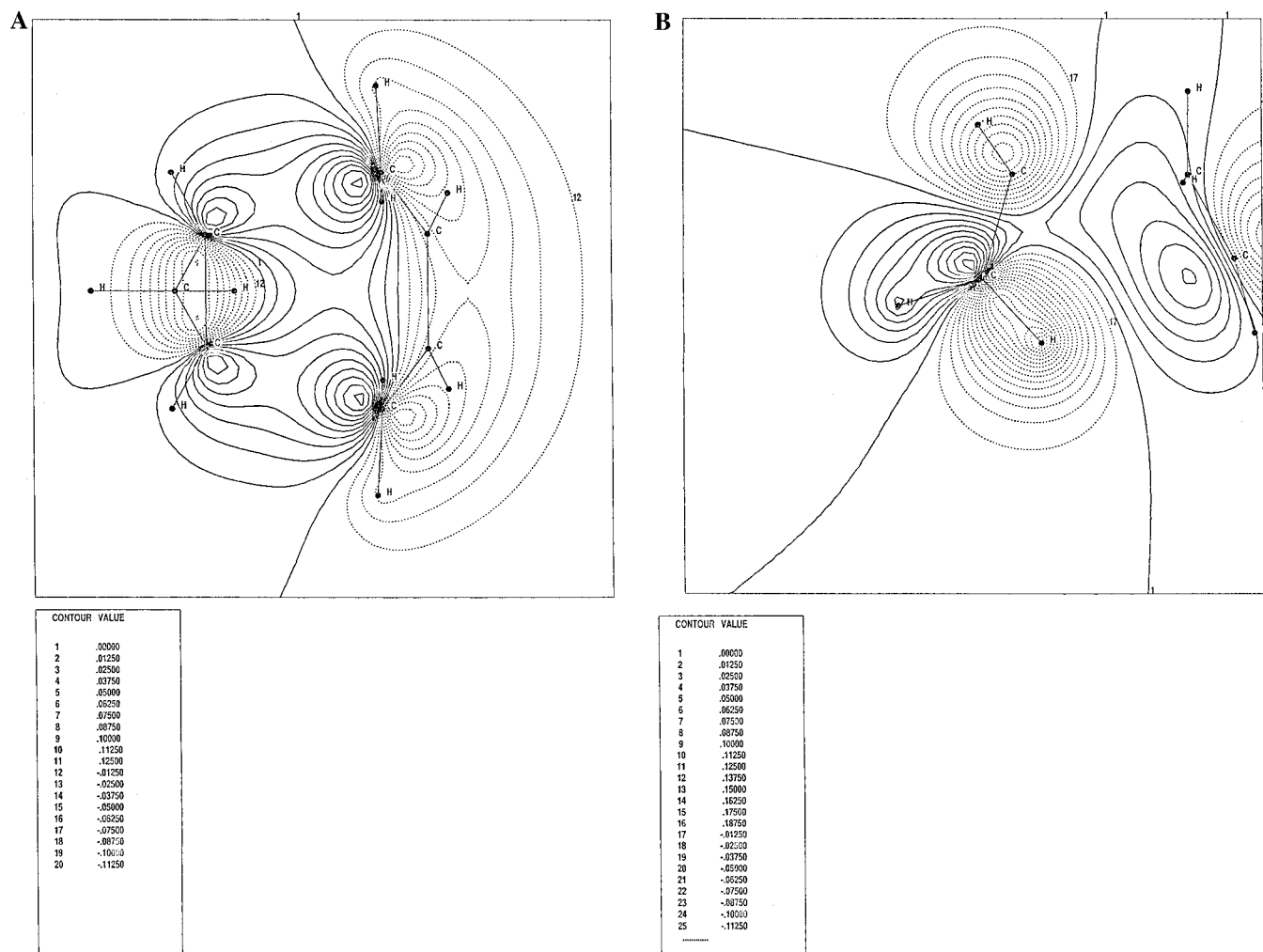
Figure 6. Contour diagram of HOMO-3 (orbital 23) (A) in the plane of the four active centers and (B) in the 2-fold symmetry plane that contains the cyclopropene CH_2.

frequency for the C−H involved. In fact, both the symmetrical and the unsymmetrical CH_2 stretches are lowered in both endo and exo transition states. The symmetrical stretch of the CH_2 decreases from 3368 in cyclopropane to 3351 and 3357 cm^{-1} in the exo and endo transition states, respectively (CASSCF/ D95). The corresponding values for the unsymmetrical stretch decrease from 3278 to 3266 and 3267 cm^{-1}. If one imagines the C−H$\cdots\pi$ vibration as composed of a weakened C−H bond, the effect would be to lower the activation energy for C−H vs C−D. However, if one considers the H$\cdots\pi$ interaction as restricting the C−H stretch, then the effect would be to raise the activation for C−H vs C−D. Since the H$\cdots\pi$ distance in the endo TS is less than that for the acetylene dimer, it seems likely that the π-bond in the TS is already buttressed against the C−H. Furthermore, unlike stable H-bonding systems, where an important vibrational mode consists of the two H-bonding entities moving away from each other, this mode will correspond to the imaginary frequency (reaction coordinate) in the endo TS. Thus, it will not contribute to the KIE.

Another contributing effect to the endo selectivity can be the differences in activation energy due to the $P\Delta V^{\ddagger}$ contribution to $\Delta G^{\ddagger}$. Reactions in solution occur under the internal pressure

$$\text{ced} = \frac{(\Delta H_{\text{vaporization}} - RT)}{V_{\text{molecular}}} \quad (2)$$

of the solvent. The cohesive energy density (ced), defined in eq 2, has sometimes been used interchangeably with the internal

solvent pressure.[45] More recently, internal pressure has taken another definition, $(dU/dV)_T$.[46] However, these quantities are not equivalent. Solvation correlations are more common with ced than with internal pressure as the former quantity is readily available from data in the *Handbook of Chemistry and Physics*. Gajewski found the rates of Diels−Alder reactions to correlate with ced.[4] The cohesive energy density of butadiene (the solvent for Baldwin's study of reaction 1) is 64 cal/cm³. The $\Delta\Delta V^{\ddagger}$ calculated by GAUSSIAN 94 (using the HF/D95* transition states) is only 0.2 cm³/mol, yielding a contribution of 0.1 kcal/ mol favoring the exo TS. This difference is much smaller than the 2.5 and 4 cm³/mol for the two examples of $\Delta\Delta V^{\ddagger}$'s of endo/ exo Diels−Alder reactions listed in a review.[47] These differences are probably due to the fact that Gaussian 94 calculates the molecular volume as the volume contained within the limits of the contour of a defined electron density (0.001 electrons/ bohr³). Such a method would not take the empty space between molecules and between nonbonded atoms in the same molecule into account. The differences between the reported $\Delta\Delta V^{\ddagger}$'s and that calculated here may be due to one or more of several factors: (1) the reactions cited in the review are different from the one studied here; (2) the experimental values are obtained under pressure where differences in the compressibilities of the

(45) Hilderbrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand: Princeton, 1970.

(46) Reichardt, C. *Solvents and Solvent Effects in organic Chemistry* 2nd ed.; VCH: Weinheim, 1988.

(47) Eldik, R. V.; Asano, T.; Le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

two TS's could affect the $\Delta\Delta V^{\ddagger}$; and (3) The error in the theoretical volume determination may exceed the $\Delta\Delta V^{\ddagger}$, itself.

Conclusions

All ab initio calculations predict that the endo product of the reaction should be favored over the exo. However, only the QCISD(T) calculations predict activation energies that are consistent with the high reaction rate. AM1 predicts the wrong endo/exo preference, but is consistent with the observed reaction rate. The preference for the endo product appears to be due to a stabilizing C−H⋯π interaction that can only occur in the endo TS. Surprisingly, CASSCF calculations do not provide significant improvement over HF for either the activation energies or the endo/exo selectivities. QCISD(T), however, predicts much more reasonable activation energies than either HF or CASSCF.

BSSE has not generally been taken into account for the calculation of the activation energies of Diels−Alder reactions. While the CP correction for this error is relatively small for HF calculations with reasonably good basis sets, this correction can be much larger in some cases. Not surprisingly, the BSSE is particularly large for small basis sets, approximately 9 kcal/mol for 3-21G. However, the large CP's calculated for the QCISD(T) activation energies are much more disturbing since recent reports have suggested that this approach leads to good activation energies for these reactions. The effect of BSSE on these results needs to be considered. Failure to correct for this error leads to fortuitously accurate results for this (3-21G) basis set. After CP correction, all the HF and CASSCF activation energies become rather similar.

Supporting Information Available: Tables giving expanded versions of Tables 1 and 2 and results of calculations on acetylene dimers as well as figures giving the geometrical guide for Table 3, extracts from outputs of CASSCF/D95V* optimized endo and exo transition state calculations, showing the complete geometries of each, and MOLDEN renderings of the contour diagrams of the electron densities of MO's 18−26 in the plane of the active centers (AC's) the cyclopropane CH2 (26 pages). See any current masthead page for ordering and Internet access instructions.