

Towards an Accurate *ab initio* Calculation of the Transition State Structures of the Diels–Alder Reaction

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Searches for the synchronous and asynchronous transition state structures for the Diels–Alder reaction of butadiene and ethylene, using a split valence 4-31G basis set, and including electron correlation, support the synchronous mechanism.

The mechanism of the Diels–Alder reaction between butadiene and ethylene presents a continuing challenge to computational theoretical chemists. There have been many theoretical studies which attempt to clarify whether this reaction proceeds *via* a synchronous or an asynchronous transition state involving, respectively, the formation of two or one new bonds. It has been suggested that methods which use the zero differential overlap approximation favour the asymmetrical transition state, whilst those methods such as *ab initio* ones, which take overlap into account, favour the synchronous reaction.¹ Thus, semi-empirical MINDO studies predict an asynchronous transition state.² However, *ab initio* studies have been limited to small basis sets, with full geometry

optimization for the synchronous transition state neglecting correlation effects,³ or partial optimization of both transition structures, with limited electron correlation included *via* configuration interaction.⁴ The need to carry out *ab initio* calculations of this reaction, with as large a basis set as possible, and to optimize the geometries with the inclusion of correlation effects is well-known.⁵ We now describe such calculations.

The computations were carried out using both a minimal STO-3G⁶ and an extended 4-31G⁷ basis. The stationary points calculated in the minimal basis were used as starting points for searches using the extended basis. The transition states were located using wavefunctions which included electron correla-

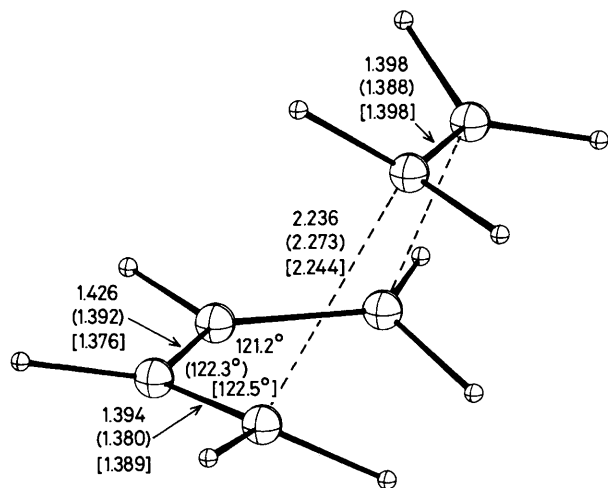
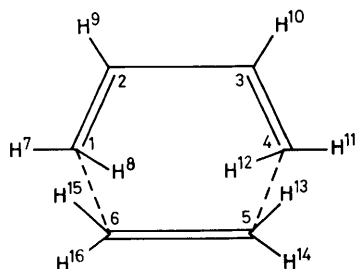


Figure 1. Calculated transition state structures for the synchronous mechanism of the Diels–Alder reaction of butadiene with ethylene. The parameters (in Å and degrees) are given for the CASSCF expansions, CAS2 and CAS1 (in parentheses) at the STO-3G level. The values in square brackets are for a 4-31G basis and a CAS1 expansion.

Table 1. Structural parameters for the synchronous 4-31G (CAS1) Diels–Alder transition state.



Bond lengths/Å		Bond angles/°		Torsional angles/°	
C ¹ C ²	1.389	C ¹ C ² C ³	122.5	C ¹ C ² C ³ C ⁴	0.0
C ² C ³	1.376	C ³ C ⁴ C ⁵	102.2	C ² C ³ C ⁴ C ⁵	57.7
C ⁵ C ⁶	1.398	C ⁴ C ⁵ C ⁶	109.1	C ³ C ⁴ C ⁵ C ⁶	49.0
C ⁶ C ¹	2.244				
		C ² C ³ H ¹⁰	118.3	C ¹ C ² C ³ H ¹⁰	169.2
C ¹ H ⁷	1.074	C ³ C ⁴ H ¹¹	119.3	C ² C ³ C ⁴ H ¹¹	172.1
C ¹ H ⁸	1.072	C ³ C ⁴ H ¹²	119.8	C ² C ³ C ⁴ H ¹²	33.9
C ² H ⁹	1.075	C ⁵ C ⁶ H ¹⁵	119.2	C ³ C ⁴ C ⁵ H ¹³	73.8
C ⁵ H ¹³	1.071	C ⁵ C ⁶ H ¹⁶	118.9	C ³ C ⁴ C ⁵ H ¹⁴	171.4
C ⁵ H ¹⁴	1.074			C ⁴ C ⁵ C ⁶ H ¹⁵	106.1
				C ⁴ C ⁵ C ⁶ H ¹⁶	105.8

tion calculated by the complete active space SCF (CASSCF) method,⁸ using both four active electrons in four orbitals (CAS1), and six active electrons in six orbitals (CAS2). The latter calculation included 175 configurations for the asynchronous mechanism. Although the use of a larger atomic basis including polarization functions would be desirable to achieve higher accuracy, such geometry optimization calculations including correlation effects are clearly not practical using a reasonable amount of present-day computing facilities.

The transition states calculated for the synchronous mechanism using the two different basis sets, and, for the minimal basis, the two different CASSCF expansions, are

shown in Figure 1. It can be seen that the structure is similar for all three calculations. We show in Table 1 the full structural data obtained for the synchronous 4-31G transition state. For the asynchronous mechanism three transition states were located using the STO-3G basis at both the CAS1 and CAS2 level corresponding to the formation of the initial carbon–carbon bond. These differed in the relative conformations of the two reacting entities. However, for the asynchronous mechanism, no transition state could be located using the more flexible 4-31G basis, in spite of extensive searches, and we do not believe this was due to inadequacies in the search procedures.

Thus our *ab initio* calculations, which were carried out using the highest level of theory feasible at the present time, point to the Diels–Alder reaction proceeding through a synchronous C_s transition state. It is to be noted that this conclusion is in disagreement with that of Dewar⁹ who suggests that multi-bond reactions cannot normally be synchronous. We have characterized the stationary point for the synchronous mechanism at the STO-3G restricted Hartree–Fock level as a true transition state having a *single* negative Hessian eigenvalue. This has been confirmed at the MC-SCF level where the Hessian has been computed in a subspace of 13 internal co-ordinates. The predicted geometry at this lower level of theory is very similar to that shown in Figure 1 and Table 1, so that at the higher levels of theory reported herein we expect the calculated structures to be transition states. Furthermore, our conclusion that the STO-3G results for the asynchronous mechanism are misleading is not surprising in view of previous MC-SCF studies of the thermal cycloaddition of two ethylenes.¹⁰ Here it was found that although in a STO-3G basis the minimum of the diradicaloid tetramethylene was well-characterized, with a substantial barrier to formation of two ethylenes, in a 4-31G basis this barrier very nearly disappeared. We conclude by noting that an experimental study of the gas phase reaction between butadiene and ethylene yielded no four-membered ring product¹¹ and this fact is in line with our finding that no asynchronous transition state exists.

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