

## A Comparison between Ethylene Dimerization and Diels–Alder Reaction

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The reaction pathways for the two reactions  $2\text{C}_2\text{H}_4 \leftrightarrow \text{C}_4\text{H}_8$  and  $\text{C}_2\text{H}_4 + \text{C}_4\text{H}_6 \leftrightarrow \text{C}_6\text{H}_{10}$  were investigated. The transition state geometries and activation energies were determined with the SINDO method and compared. Both reactions were found concerted with different significance of diradical character at the transition state. Whereas the ethylene dimerization showed that a diradical will be encountered along the reaction pathway, we did not find one in the Diels–Alder reaction.

**Key words:** Cycloaddition reactions

### 1. Introduction

Recent years have seen an increase in semiempirical and *ab initio* calculations of chemical reactions in the gas phase. Authors claim not only qualitative, but quantitative accuracy in predictions of activation energies and transition state geometries. Whereas the former allow us to compare with experimental data, the latter are in general inaccessible to experimental investigation. So a basis for support of a calculated structure can be given only indirectly through explanation of the mechanism of a chemical reaction (concerted versus two-step) or through the expected accuracy of the method (SCF versus CI, *ab initio* versus semiempirical). Controversies arise when within the claimed accuracy limits of the various methods results appear which contradict each other. Two simple cycloaddition reactions are of such a nature: the ethylene dimerization and the Diels–Alder reaction. In the first case the question was concerted versus two-step [1] and  $(2_s + 2_s)$  versus  $(2_s + 2_a)$  pathway [2]. Calculations supported the concerted pathway, but favoured contrary to Woodward–Hoffmann the forbidden  $(2_s + 2_s)$  pathway slightly [3]. At that time we had applied a limited optimization and did not determine the geometry

of the transition state, so the question of the importance of diradical character was not answered. At about the same time Dewar and Kirschner [4] published a study on the ethylene dimerization emphasizing the diradical character of the transition state. In the second case a number of contradictory results were obtained which Houk and collaborators [5] took to force the issue between semiempirical and *ab initio* methods. MINDO/3 calculation [6] predicted a highly unsymmetrical transition state with biradicaloid character, whereas two *ab initio* calculations [7, 8] obtained a symmetrical transition state based on a synchronous concerted reaction.

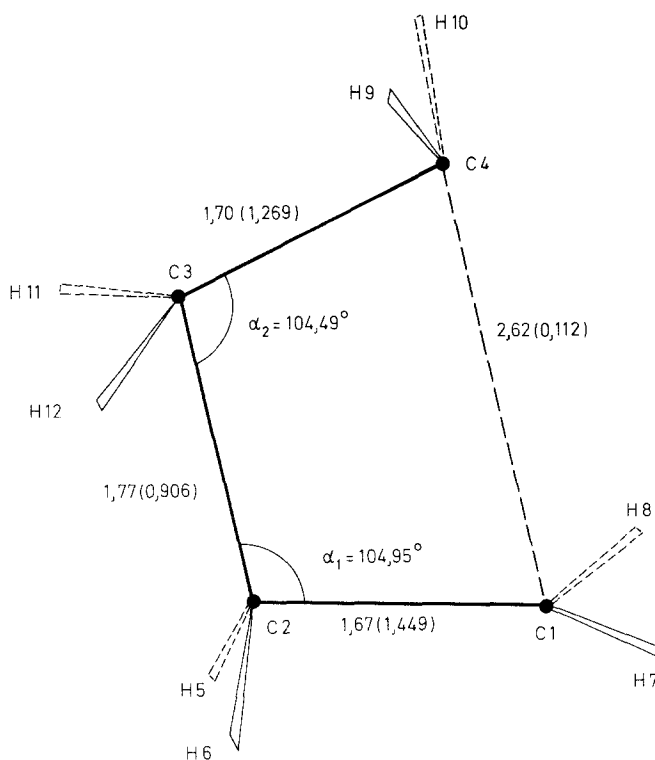
In this paper we want to contribute towards the solution of this controversy by an alternative semiempirical method SINDO [9] which was proven to be qualitatively successful in chemical reactions of the kind mentioned above. In the following sections we present activation energies and transition state geometries for the two dimerizations and compare these with the results in the literature. We suggest that a major difference exists between the two reactions which can be shown by bond order considerations.

## 2. The Ethylene Dimerization

First, we optimized ethylene and cyclobutane with the SINDO method on the SCF level. Then CI was used with the lowest single and the two lowest double excitations for possible MO level crossings. We found that bond lengths are overestimated by 10% and that the relative binding energies are correct within 20%. This is what we expected from the statistics performed previously [9]. The close agreement between our calculated  $\Delta H_R = 22$  kcal/mole with the experimental value of 18 kcal/mole encouraged us to proceed with the search for a reaction pathway. We took the distance between two C atoms of the two ethylene molecules as a guiding coordinate. We minimized the energy with respect to all other internal coordinates in intervals of 0.05–0.3 Å between 1.70 and 3.4 Å. The transition state was found by stabilizing one negative root of the eigenvalues of the force constant matrix. This is due to the fact that at a saddle point there is one direction with a negative curvature of the potential surface whereas all other directions have a positive curvature. The geometry of the transition state given in Fig. 1 was obtained by variation of all internal coordinates. To have a proper idea about the situation the CC bond lengths need to be reduced by 10%. From a bond order concept recently advocated [10] we obtained the bond orders given in parentheses. There is a formation of almost a single bond between the approaching atoms C2 and C3 whereas the second bond has only slightly begun to form. The double bond character of the CC bonds in the ethylene molecules is not much retained. To address ourselves to the question of diradical character we introduce the idea of a valence number  $N$  for an atom.  $N$  is the sum of all bond orders of an atom to adjacent atoms in the molecule. The difference between the valence numbers of two atoms

$$\Delta N = N_A - N_B = \sum_{C \neq A} P_{AC} - \sum_{C \neq B} P_{BC} \quad (2.1)$$

should be a measure of how different the strength of overall bonding is at these atoms. We have taken the average of valence numbers of the atom pairs (C2, C3)



**Fig. 1.** Geometry and bond orders for the transition state of  $2 \text{C}_2\text{H}_4 \leftrightarrow \text{C}_4\text{H}_8$ ; bond lengths in Å, bond orders in parentheses

and (C1, C4) of Fig. 1 and plotted  $\Delta N$  in Fig. 2 along the reaction pathway. Since bond C2C3 is forming faster than the bond C1C4,  $\Delta N$  is increasingly positive. Coming from two ethylenes,  $\Delta N$  has a maximum of 0.76 just before the transition state is reached. Here the value has dropped to 0.49. Our conclusion is that a significant amount of diradical character can be encountered along the reaction pathway. But the transition state is not a diradical. It does not even have a maximum of diradical character. We would expect a true diradical in a cycloaddition reaction to have a  $\Delta N \approx 1$ . Our conclusion seems to be supported by the result that we do not obtain a singlet–triplet degeneracy at the transition state, but that the triplet is substantially lower in energy. Due to the lack of singlet–triplet degeneracy the subsequent CI calculation did not lower the activation energy at the transition state by more than 0.1 kcal/mole. Our conclusions are similar to Dewar's [6] that the transition state is unsymmetrical, but vary from his statement that a biradicaloid ridge is most significant for this reaction. There is no free rotation of the C1H7H8 group. We find a barrier of rotation of 12 kcal/mole about the C1C2 bond. To illustrate this reaction further, we have taken a cross section through the potential surface by varying bond angles C1C2C3 and C2C3C4 symmetrically and bond length C2C3. We find that the change of a bond length and bond angles is synchronous but with different velocity between cyclobutane

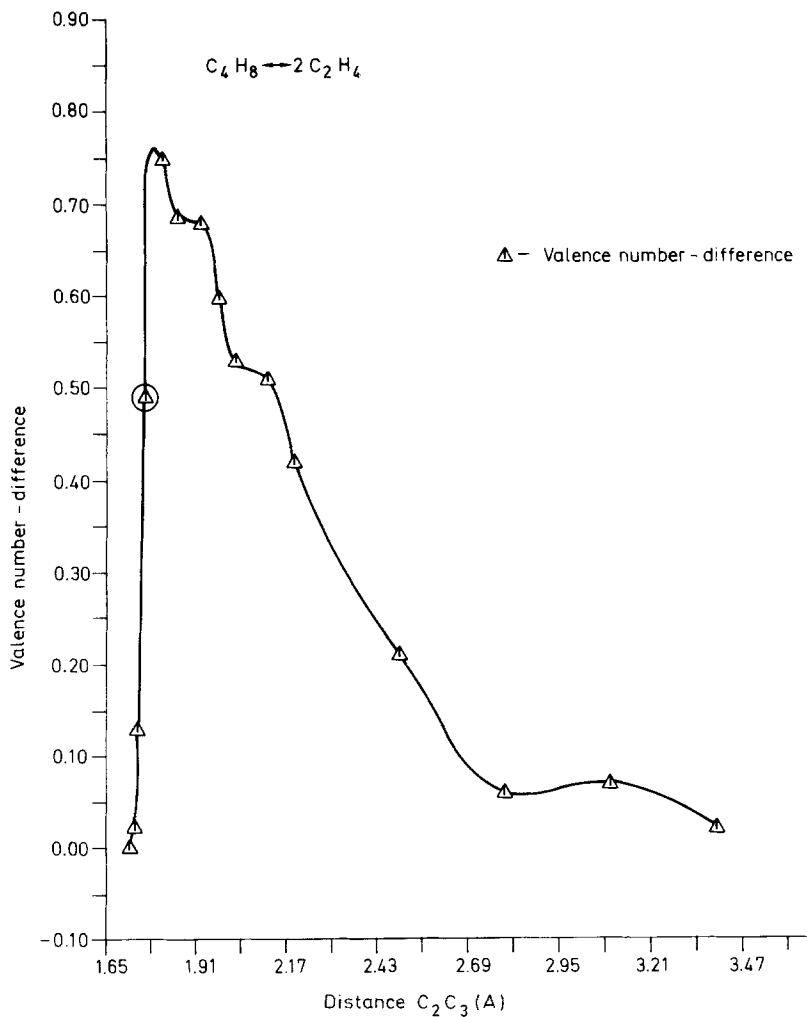


Fig. 2. Valence number difference for  $2 C_2H_4 \leftrightarrow C_4C_8$ ; transition state encircled

Table 1. Heat of reaction and activation energies for  $A + A \leftrightarrow B$  (A = ethylene, B = cyclobutane)

Author, method	$\Delta H_R$ (kcal/mole)	$E_A$ (kcal/mole)	
		A + A $\leftrightarrow$ B	B $\leftrightarrow$ A + A
Experimental [11, 12]	18.0	44.5	62.5
Dewar, MINDO/3 [4, 13]	43.5	18.5	62.0
This work, SINDO [9]	22.0	54.5	76.6
Salem, <i>ab initio</i> [14]	28.0	128.0	156.0
Segal, <i>ab initio</i> [15]	35.3	42.4	77.7

and the transition state. The angles open faster than the bond length increases up to the transition state. It should also be observed that the carbon framework of the transition state is planar, thus favouring a ( $2_s + 2_s$ ) pathway. In Table 1 we finally present a comparison of our energy data with experimental [11, 12] and various semiempirical [13] and *ab initio* calculations [14, 15]. We will only remark here that heats of reaction and activation energies are as good or better than those in the literature. We find that a singlet–triplet degeneracy exists close to the transition state as Segal did. But there is no intermediate as a true minimum on the hypersurface as in Segal’s case. Of course, Segal did not diagonalize the whole force constant matrix for all internal coordinates.

### 3. The Diels–Alder Reaction

After full optimization of reactants and products, we proceeded as in the previous section to generate the reaction pathway for the reaction butadiene + ethylene  $\leftrightarrow$  cyclohexene. To determine the transition state all internal coordinates were varied. A limited CI calculation was performed subsequently as in the ethylene dimerization. The energy results in the following are based on CI. The geometry of the transition state is presented in Fig. 3. Again one has to subtract 10% from the obtained bond lengths to get the real idea of these results. The situation is unsymmetrical as in Dewar’s case [6] but the unsymmetry is much less pronounced. The shorter bond length C4C11 is characterized by a very small positive bond order, the larger one C3C12 is still repulsive. Ethylene has its CC bond order barely reduced by 0.04. The single bond order of butadiene has increased slightly by 0.02, the double bond orders have been reduced by 0.04 and 0.06. This situation is entirely different from the ethylene dimerization, where a single bond has been substantially formed. Here is where we differ greatly from Dewar’s result who

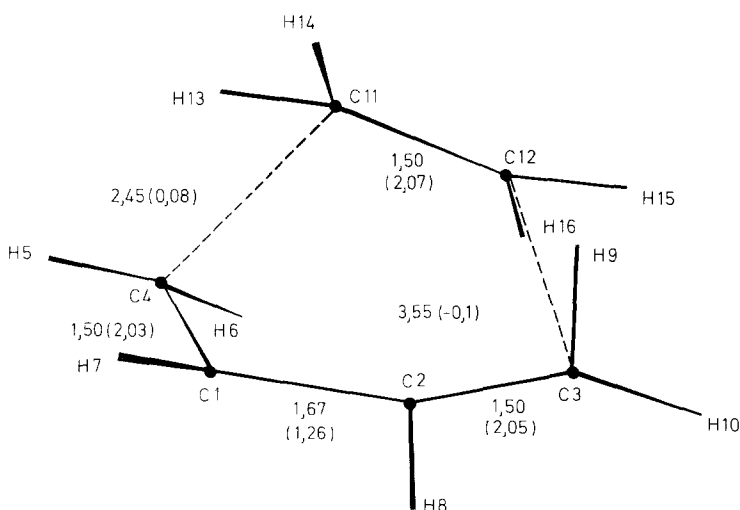


Fig. 3. Geometry and bond orders for the transition state of  $C_2H_4 + C_4H_6 \leftrightarrow C_6H_{10}$ ; bond lengths in Å, bond orders in parentheses

again finds one substantial bond formed between the fragments at the transition state. In Fig. 4 we see that the valence number difference between the average of atom pairs (C4, C11) and (C3, C12) is much less pronounced than in the ethylene dimerization. The encircled transition state here is between the fragments and the maximum of the curve. Also the singlet energy is lower than the triplet energy at the transition state. This clearly means that a diradical is even less important for this reaction than for the ethylene dimerization. To characterize the various possibilities for the transition state we present Fig. 5. Ethylene dimerization belongs to case c), the Diels–Alder reaction to case a). Dewar finds in both cases that situation b) is characteristic.

Finally we present again the energy data in Table 2. Experimental data [11, 16]

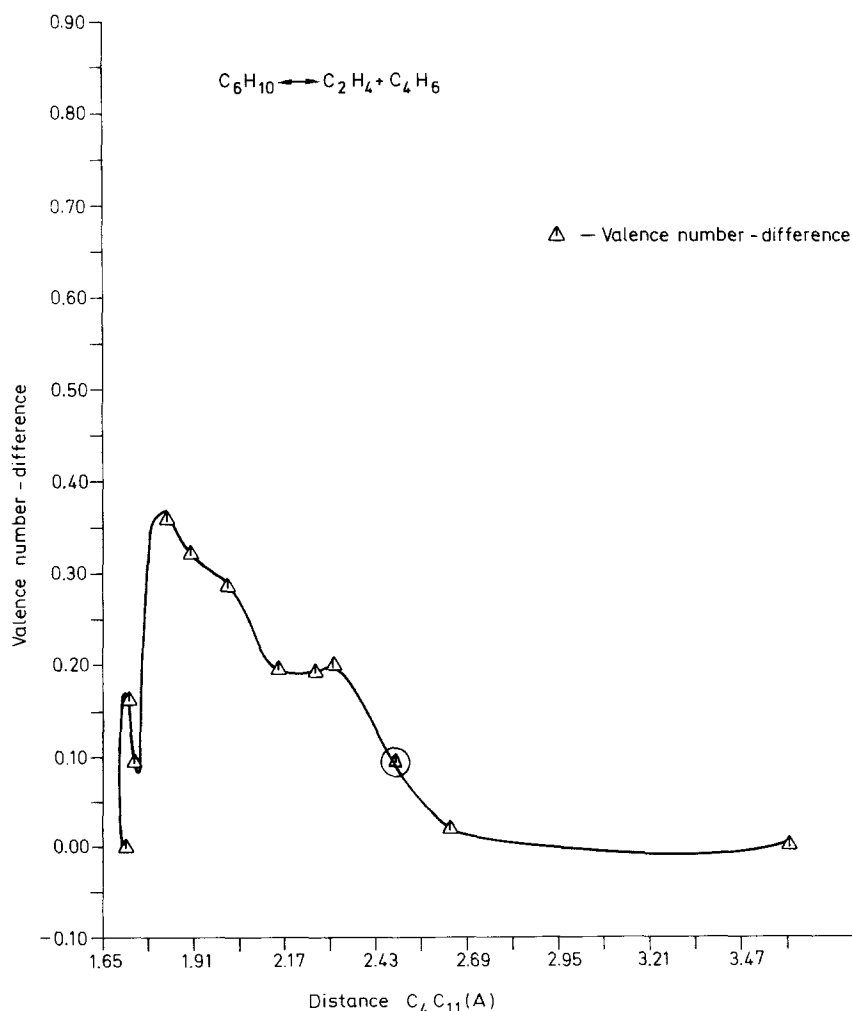
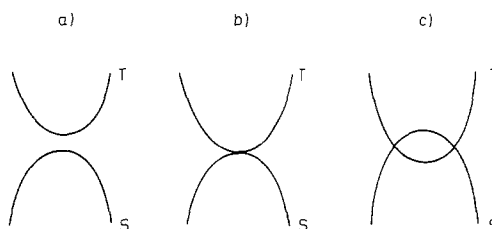


Fig. 4. Valence number difference for  $C_2H_4 + C_4H_6 \leftrightarrow C_6H_{10}$ ; transition state encircled



**Fig. 5.** Various relative stabilities of singlet and triplet states in the transition state region

**Table 2.** Heat of reaction and activation energies for  $A + B \leftrightarrow C$  ( $A =$  butadiene,  $B =$  ethylene,  $C =$  cyclohexene)

Author, method	$\Delta H_R$ (kcal/mole)	$E_A$ (kcal/mole)	
		$A + B \leftrightarrow C$	$C \leftrightarrow A + B$
Experimental [11, 16]	39.6	66.9	27.5
Dewar, MINDO/3 [6, 13]	51.2	79.4	28.2
This work, SINDO [9]	38.5	48.8	10.4
Salem, <i>ab initio</i> [7]	37.3	79.6	42.6
Leroy, <i>ab initio</i> [8]	106.4	127.2	20.8

are again compared with our and other semiempirical [6, 13] and *ab initio* results [7, 8]. Although our agreement with experimental data is less satisfactory than in the ethylene dimerization because of a too low activation energy, the *ab initio* results are not really better either. In this case Dewar's overall agreement is apparently the best. But his error in  $\Delta H_R$  is again quite pronounced. We do not think that a conclusion from these data can be drawn as to the quality of the transition state geometry. In the light of a recent investigation by Basilevsky *et al.* [17], serious doubts are cast on MINDO/3 calculations on chemical reactions, since certain energy integral approximations appear to be improper at next-neighbour distances.

#### 4. Conclusion

We have documented that there is a remarkable difference between the ethylene dimerization and the Diels-Alder reaction. Whereas the latter has an early transition state with slight unsymmetry, the former one has a late transition state with one bond apparently formed. Although both reactions appear concerted, the diradical character seems more pronounced during the ethylene dimerization. We obtained this result by the comparison of singlet and triplet state energies at the transition state and by the difference of valence numbers during the course of these reactions.

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