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Theoretical Study of the Diels-Alder Reaction

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The cycloaddition of ethylene to butadiene has been studied by the *ab initio* LCAO-SCF-MO method of Roothaan using STO-3G and 7*s*-3*p* basis sets.

The potential energy hypersurface of the supersystem formed by the reactants has been calculated in order to determine the reaction path. It was found that, during the approach of the partners, the planes of the molecules form an angle around 70°.

The activated complex has a geometry which prefigures the half-chair conformation of cyclohexene and exhibits no biradical character. Our theoretical results are in reasonable agreement with the corresponding experimental ones.

Key words: Diels-Alder reaction – Cyclohexene

1. Introduction

The Diels-Alder cycloaddition is an important reaction in organic chemistry. Although high pressure kinetic studies have demonstrated the concerted character of the reaction [1], the theoretical interpretation of its mechanism still remains in controversy [2]. In this present work we study the cycloaddition of ethylene to butadiene in order to specify the reaction path and to characterize the transition state.

2. Method

All calculations have been carried out by the *ab initio* LCAO-SCF-MO method of Roothaan. For the transition state geometry the minimal basis set STO-3G was chosen [3]. However, several points on the hypersurface, i.e. the isolated reactants, the activated complex, and cyclohexene, have been recalculated using a medium sized contracted gaussian basis set (7*s*-3*p*) [4] which gives better results in point of view of energy. The calculations were accomplished through a modified version of the GAUSSIAN-70 program [5] which permits the construction of localized orbitals through the processes of Boys [6] and Magnasco-Perico [7].

3. Results and Discussion

3.1. Geometry Optimization

The geometric parameters were first varied to give the minimum total energy

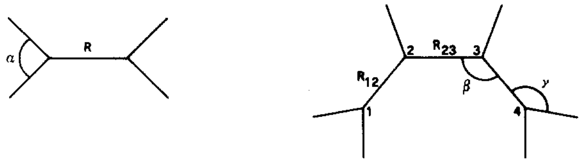


Fig. 1. Geometric parameters for ethylene and butadiene

Table 1. Optimized geometric parameters

Ethylene		Butadiene			
R(Å)	α(°)	R_{12}(Å)	R_{23}(Å)	β(°)	γ(°)
1.310	117	1.314	1.497	123	120

for ethylene, butadiene and cyclohexene. The results obtained for these three molecules are given as follows.

3.1.1. The Reactants

Ethylene and butadiene have been optimized with respect to the parameters given in Fig. 1. The values found are collected in Table 1. All CH bond lengths were taken as 1.07 Å. The difference in total energy for these geometries as compared to that found for experimental geometries is 1 kcal/mole for ethylene and 1.5 kcal/mole for butadiene using both the STO-3G and 7*s*-3*p* basis sets.

3.1.2. Cyclohexene

In this case we have adopted the lengths and angles for the half-chair form found by electron diffraction [8]. However, the transition state of the cycloaddition was found to have an immediate form between that of the half-chair and the boat. The boat and two intermediate conformations have therefore been calculated for cyclohexene using the geometries found by Bucourt and Hainaut (Fig. 2) [9]. The sign of the dihedral angle formed by the two adjacent CC bonds on each CC bond is also given [8, 9]. The total and relative energies calculated for the four conformations are found in Table 2. These results are also compared with those of Bucourt and Hainaut obtained through a semi-empirical method of "deformation energy" calculations [9]. We have found, as well as these authors, that the half-

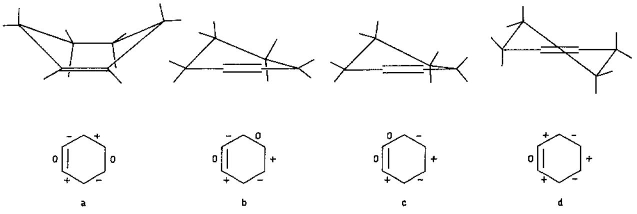


Fig. 2. Conformations of cyclohexene

Table 2. Energies of the conformations of cyclohexene

Conformation	E_T(a.u.)	ΔE (STO-3G) kcal/mole	ΔE [9] kcal/mole
a	−230.244512	6.90	6.93
b	−230.246418	5.69	4.87
c	−230.252874	1.64	1.21
d	−230.255489	0.00	0.00

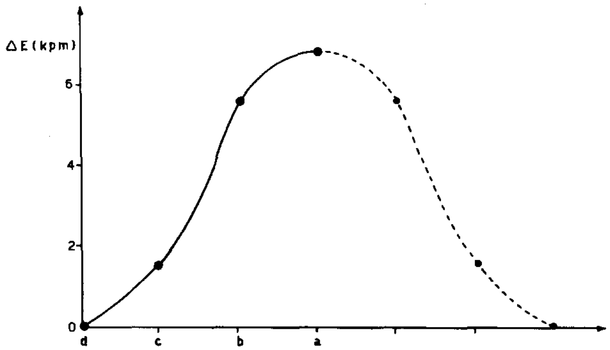


Fig. 3. Potential energy curve for cyclohexene

chair form is the most stable and the boat form the least stable. The evolution of the total energy of cyclohexene from the half-chair to the boat conformation is given in Fig. 3.

3.2. Potential Energy Hypersurface

The total energy of the ethylene-butadiene supersystem has been calculated as a function of geometric parameters given below. It was found that a coplanar approach for the reactants was energetically very unfavourable; and, as the symmetry of the problem suggests, it was found that the distances between the corresponding terminal carbons of the two molecules remain equal during the reaction. In addition, the non-coplanar approach of the two partners can be characterized by three directional parameters defined in Fig. 4, *viz.* R_{16} (or R_{45}): distance between the corresponding terminal carbons being joined; α: the angle formed by the normal of the ethylene plane and the plane of the butadiene molecule; β: the rotation angle of the ethylene around the axis of approach ($\beta = 0$ if C_1C_4 is parallel to C_5C_6). Furthermore, it was found that the plane of the ethylene molecule remains perpendicular to the axis of approach. From these variables the reaction coordinate can therefore be chosen as the distance R_{16}.

In addition to the directional parameters, the following geometric parameters were also varied to optimize the total energy as a function of R_{16}: the bond lengths R_{12}, R_{23} and R_{56}; the dihedral angle δ formed by the plane perpendicular to the

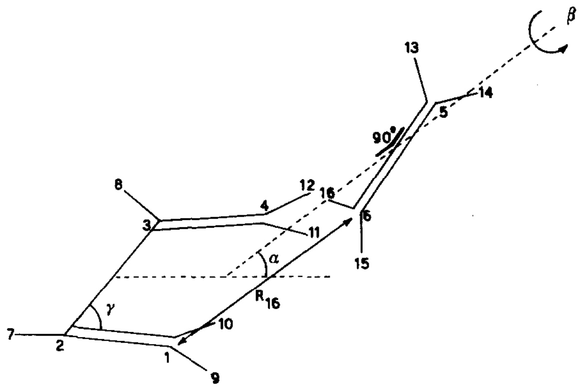


Fig. 4. Geometric parameters used in the calculations

axis of approach and the plane $C_5C_6H_{16}$ (or $C_5C_6H_{14}$); the angle ε formed by the plane perpendicular to the axis of approach and the plane $C_5C_6H_{13}$ (or $C_5C_6H_{15}$); the dihedral angle μ formed by the plane of the butadiene carbons and the plane $C_1C_2H_{10}$; and the dihedral angle ν formed by the butadiene plane and the plane $C_3C_4H_{11}$. Within ±2° the atoms H_9 and H_{12} remain in the same pseudo-equatorial position during the reaction. As might be expected, the atoms H_7, C_2, C_3 and H_8 are also coplanar throughout the entire reaction. These parameters are also shown in Fig. 4. The precision obtained for the distances is estimated to ±0.02 Å and that for the angles ±2°.

Table 3 unites the values of the parameters corresponding to the energy minima for the hypersurface defining the reaction path given in Fig. 5. The ordinate gives the relative energy of the supersystem (in kcal/mole) chosing as zero the sum of the energies for the isolated reactants. It is to be noted that nearly 120 points of the hypersurface have been calculated in order to obtain the results of Table 3.

3.3. Population Analysis along the Reaction Path

3.3.1. Bond Overlap Population

Table 4 gives the bond overlap populations [10] for the same points found in Table 3. It is found that before reaching the transition state the populations for the two partners vary little and that the populations for the bonds in formation become appreciably positive only in neighborhood of the activated complex.

In Table 5, we translate these results into bond energy terms by using the relation [11]:

$$\mathrm{E}_{AB} = a_{AB}P^3{}_{AB} + b_{AB}P^2{}_{AB} + c_{AB}P_{AB}\ \text{(kcal/mole)},$$

where E_{AB} is the energy of the bond in question and P_{AB} is its overlap population in the STO-3G basis set. The constants a, b, and c equal respectively 216.722, −263.308, and 53.653 for the CC bond. As soon as the activated complex is passed, the bond overlap populations rapidly evolve towards the values calculated for cyclohexene.

Table 3. Geometric parameters for several points on the reaction path

State	$R_{16}=R_{45}$(Å)	R_{12}(Å)	R_{23}(Å)	R_{56}(Å)	α(°)	β(°)	γ(°)	ε(°)	δ(°)	μ(°)	ν(°)	E_T(a.u.)
I	5.000	1.314	1.497	1.310	—	—	123	0	0	0	0	−230.085892
II	3.167	1.314	1.497	1.310	72	0	123	0	0	0	0	−230.084749
III	2.867	1.314	1.497	1.310	72	0	123	0	0	0	0	−230.075017
IV	2.567	1.314	1.497	1.310	72	0	123	0	0	0	0	−230.054812
V	2.367	1.314	1.497	1.310	72	0	123	5	5	5	5	−230.027147
VI[a]	2.167	1.350	1.455	1.350	66	5	123	12	8	22	25	−230.014856
VII	1.967	1.400	1.400	1.410	62	10	123	24	16	40	45	−230.067077
VIII[b]	1.504	1.504	1.325	1.542	0	15	122	0	120	75	135	−230.255489

[a] Transition state

[b] Half-chair conformation of cyclohexene

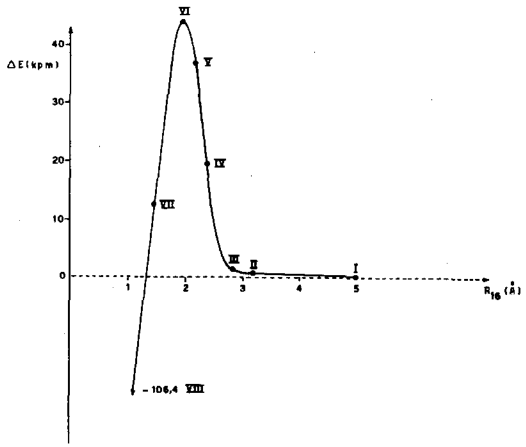


Fig. 5. Reaction path for the cycloaddition of C_2H_4 to C_4H_6

Table 4. Bond overlap populations (STO-3G Basis set)

	C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_6	C_6–C_1
I	0.6016	0.4006	0.6016	0.0000	0.6100	0.0000
II	0.6017	0.4007	0.6017	0.0000	0.6095	0.0000
III	0.6008	0.4030	0.6017	−0.0004	0.6093	−0.0004
IV	0.5993	0.4071	0.5993	−0.0020	0.6090	−0.0020
V	0.5936	0.4153	0.5936	0.0028	0.6021	0.0028
VI[a]	0.5436	0.4659	0.5431	0.0648	0.5438	0.0635
VIII	0.4490	0.5486	0.4524	0.1924	0.4442	0.1943
VIII	0.3781	0.6053	0.3781	0.3641	0.3596	0.3641

[a] Transition state

Table 5. Bond energies (kcal/mole)

	C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_6	C_6–C_1
I	140.5	89.9	140.5	0.0	142.5	0.0
II	140.6	89.9	140.6	0.0	142.4	0.0
III	140.4	90.5	140.4	—	142.3	—
IV	140.0	91.6	140.0	—	142.2	—
V	138.7	93.7	138.7	0.4	140.7	0.4
VI[a]	126.5	106.8	126.4	11.0	126.6	10.8
VII	102.5	127.8	103.3	37.8	101.2	38.2
VIII	84.0	141.4	84.0	80.4	79.2	80.4

[a] Transition state

Table 6. Atom charges and charge transfer[a] (STO-3G Basis set)

State	C_1	C_2	C_3	C_4	C_5	C_6	$t_{C_2H_4}$
I	−0.1231	−0.0588	−0.0588	−0.1231	−0.1262	−0.1262	0.0000
II	−0.1225	−0.0591	−0.0591	−0.1225	−0.1212	−0.1212	0.0002
III	−0.1203	−0.0594	−0.0594	−0.1203	−0.1210	−0.1209	−0.0040
IV	−0.1175	−0.0609	−0.0609	−0.1175	−0.1234	−0.1234	−0.0126
V	−0.1151	−0.0622	−0.0622	−0.1151	−0.1279	−0.1279	−0.0270
VI[b]	−0.1063	−0.0670	−0.0695	−0.1066	−0.1291	−0.1250	−0.0253
VII	−0.1092	−0.0658	−0.0765	−0.1097	−0.1148	−0.1072	0.0194
VIII	−0.1062	−0.0633	−0.0633	−0.1062	−0.0931	−0.0931	—

[a] Charge transfer is defined as follows: $\left(\sum_{i\varepsilon C_2H_4} q_i\right)$.

[b] Transition state.

3.3.2. Net Charges

In Table 6 an accumulation of electrons is observed for carbons 2, 3 and to a lesser extent 5. In return, carbons 1 and 4 become poorer in electrons. Furthermore, a charge transfer can be evaluated from one partner to the other during the course of reaction by the relation [12]:

$$t_{C_2H_4}=\sum_A q_A$$

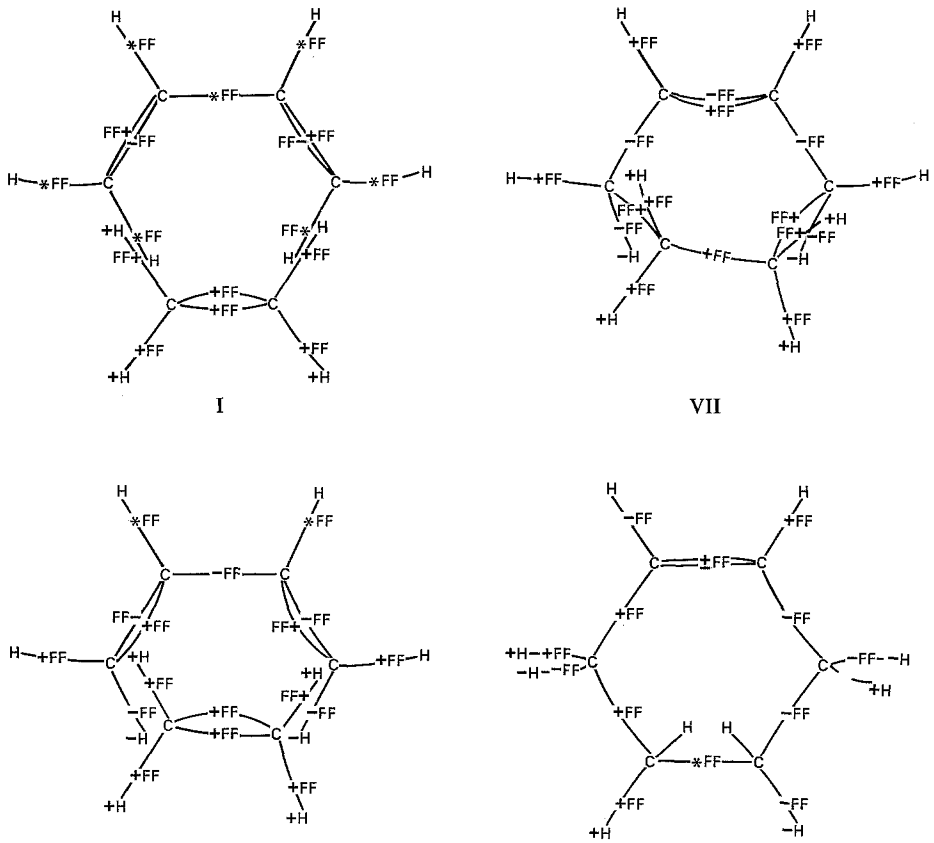
This value is listed in the last column of Table 6. A slight transfer of charge from butadiene to ethylene was found to be maximum in the proximity of the transition state. One can therefore see that an electron withdrawing group on ethylene would favor this reaction.

3.4. Analysis of the Transition State

The properties of the transition state have also been calculated using a basis set which permits a better evaluation of total energies, i.e. Clementi's basis of contracted gaussians 7*s*-3*p*. With this basis set the total energies for the reactants, the activated complex, and cyclohexene equal −77.636478 a.u. (C_2H_4), −154.195913 a.u. (C_4H_6), −231.799172 a.u., −231.976093502 a.u. respectively. This gives an activation energy of 20.8 kcal/mole.

The activated complex has also been described in terms of localized orbitals for different points on the reaction path. The localization process of Foster and Boys [6] specifies the number and nature of the bonds in a molecule and calculates the positions for the centroids of the negative charges associated with these bonds. These bonds are schematized in Fig. 6 for different points along the reaction path; the positions of the centroids of charge are also indicated.

Until the activated complex the number and nature of the localized orbitals remain unchanged. However, a separation of the centroids is observed in each double bond. When the activated complex is passed, a complete reorganization of the centroids was seen to form two single bonds between the two reactants and a double bond between carbons 2 and 3. This situation is very close to that seen in cyclohexene.



I VII VI VIII

Fig. 6. Evolution of the centroids along the reaction path. I) $R=5$ Å VI) $R=2.17$ Å VII) $R=1.97$ Å VIII) Cyclohexene

4. Conclusions

This work has allowed us to explore a mechanism for the Diels-Alder reaction, which, until present, has never been studied systematically by an *ab initio* process. The following conclusions can be taken from this work.

1. During the approach of the partners, the angle between the axis of approach of the ethylene and the plane of the butadiene remains around 70°.
2. The transition state has a geometry which prefigures the half-chair conformation of cyclohexene. This totally optimized form was found to be 1.2 kcal/mole more stable than the optimized boat configuration of the transition state ($\beta=0°$, $\delta=\varepsilon=10°$); this value can be seen to fit into the context of the half-chair boat transition for cyclohexene given in Table 2. Furthermore, the bond lengths were found to be the same for both these forms of the transition state; this retention of bond lengths could only be assumed in empirical methods such as that of Bucourt and Hainaut [9].

3. During the formation of the activated complex a slight transfer of charge is observed from the butadiene to the ethylene.
4. The theoretical activation barrier (20.8 kcal/mole) is in reasonable accord with the corresponding experimental value (25.1 kcal/mole) [13].
5. As generally found in the method of Roothaan, the heat of reaction is overestimated, -106.4 kcal/mole in basis STO-3G and -90.1 kcal/mole in basis $7s$-$3p$ (experimental, -67.6 kcal/mole [14]). It is quite normal to calculate a barrier of activation more precisely than a heat of reaction since the electronic configuration usually changes little between the reactants and the activated complex. Furthermore, the formation of the product is accompanied by a profound reorganization of the bonds which in return causes an important modification of the correlation energy of the supersystem.

These results also present an excellent accord with those found by high pressure kinetic studies [1], in particular the geometry of the activated complex and the concerted character of the addition. However, our conclusions are not in accord with those of Dewar [2], for the transition state that we obtained tends towards an equal distance between the terminal carbons C_1–C_6 and C_4–C_5 and therefore away from any biradical character.

It is evident that our results cannot be generalized for all Diels-Alder reactions especially those where the dipolarophile contains strong electron withdrawing groups.

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