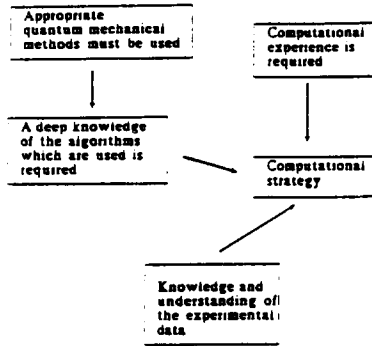


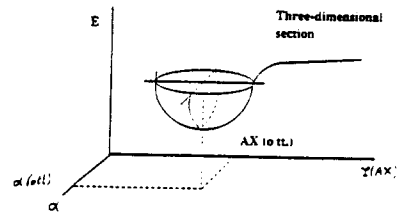
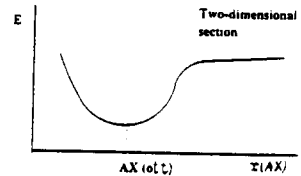
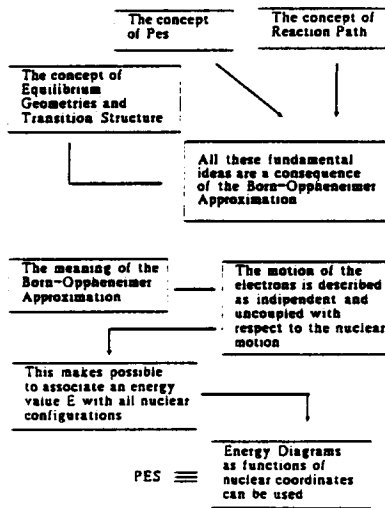
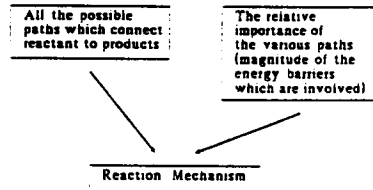
An automatic tool (black box) to compute a reaction mechanism does not exist ————— computational strategy needed



A few fundamental concepts:

The concept of potential energy surface (PES) associated with a chemical reaction

What can you get from a PES:



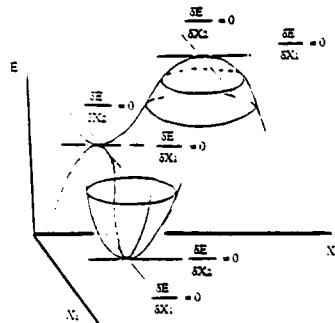
Relevant points on a PES

All the relevant points on a PES are stationary points

First Derivatives of the Energy with respect to nuclear coordinates (forces) are zero:

$$\frac{\partial E}{\partial X_i} = 0 \quad (i = 1, 2, \dots, 3N-6)$$

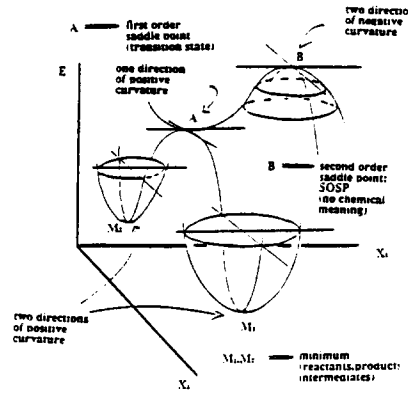
In topology stationary points are known as critical points



**Important Statement:**

Not all the critical points on a PES have chemical meaning

Consequently, after having found a critical point on a PES, you must also determine very carefully its nature



The nature of a critical point can be found easily if one can compute the force constant matrix with respect to the nuclear coordinates

The force constant for coordinate  $X_1$

$$\frac{\partial^2 E}{\partial X_1^2} \quad (\text{Second Derivative of the energy})$$

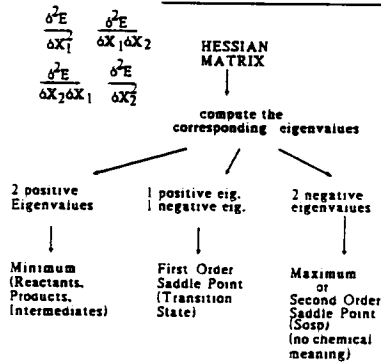
A 2 Dimensional case  $E = E(X)$  → Trivial solution

compute  $\frac{\partial^2 E}{\partial X^2}$

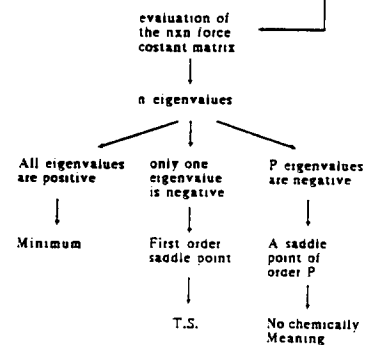
$$\frac{\partial^2 E}{\partial X^2} > 0 \rightarrow \text{Min.} \quad \frac{\partial^2 E}{\partial X^2} < 0 \rightarrow \text{Max.}$$

A 3 - Dimensional case:  $E = E(X_1, X_2)$

The full second energy derivative matrix (hessian) is required. The corresponding eigenvalues must be computed



3 - dimensional case → Easy to extend to the n - dimensional case  $n = 3N - 5$



The computational strategy which is employed is completely general

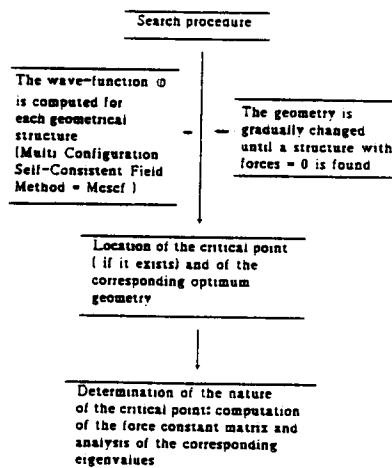
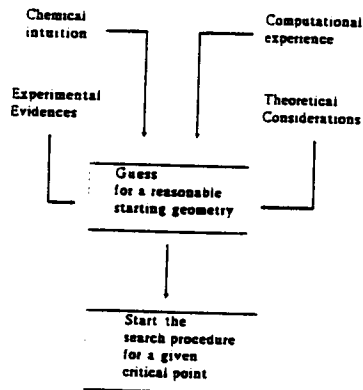
In principle you can get a complete 'a priori' analysis of the PES

in practice a too large number of computations is required to do that

This makes a full 'a priori' analysis too expensive for reactions of chemical interest

Consequently — in a 'routine' investigation of a chemical reaction it is convenient to perform the search for the various critical points (and the optimization of the corresponding geometrical structures) in some restricted areas of the Pes

Factors which allow to choose the important restricted areas of the PES and to guess reasonable starting geometries for the critical points

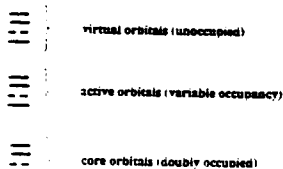


QUANTUM MECHANICAL METHOD USED

MC-SCF (multi-configuration self-consistent field)

$$\Psi = \sum_i C_i \Phi_i$$

CSF (configuration state functions)



CAS (complete active space)  
all possible configurations arising from the valence space

MC-SCF ——— Non-dynamic correlation energy (structure dependent)

Good description in the transition region

MCSCF/MP2 (single computations on geometries optimized at the mc-scF level)

Dynamic correlation energy

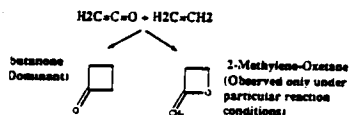
Very important for the computation of activation energies

Basis sets

Minimal basis set (sto-3g) for exploratory work

Extended basis sets for an accurate computation of geometries and energies

CYCLOADDITION REACTION BETWEEN KETENE + ETHYLENE

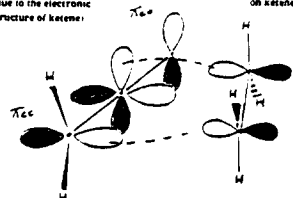


Experimental Interest: Prototype Reaction for an important class of Reactions

CUMULENES - OLEFINS

An important synthetic tool to obtain cyclic compounds

**THEORETICAL INTEREST**  
 (due to the electronic structure of ketene)



Simple MO concepts suggest:

Possibility for a supra-antara attack (suprafacial approach for ethylene, antarafacial approach for ketene)

The most popular hypothesis is the mechanism of this reaction

This possibility has never been tested quantitatively

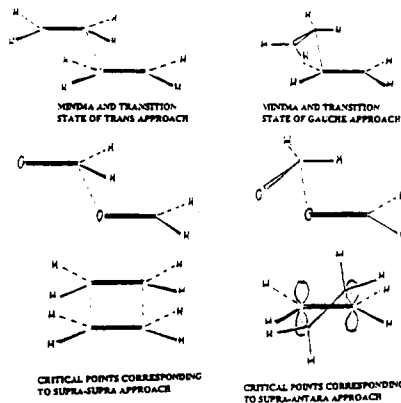
In agreement with experimental data (kinetic and stereochemical evidence) which suggest a concerted mechanism.

THE STRATEGY WHICH HAS BEEN USED TO STUDY THE REACTION OF KETENE + ETHYLENE IS BASED ON THE ANALOGOUS CYCLOADDITION REACTIONS

ETHYLENE + ETHYLENE

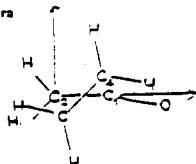
FORMULENDE I - FORMULENDE II

CRITICAL POINTS ON THE PES

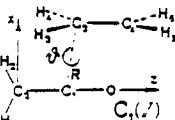


APPROACHING DIRECTIONS

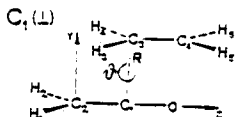
(a) supra-antara



(b) THE APPROACHING DIRECTION LIES IN THE PLANE OF THE KETENE MOLECULE

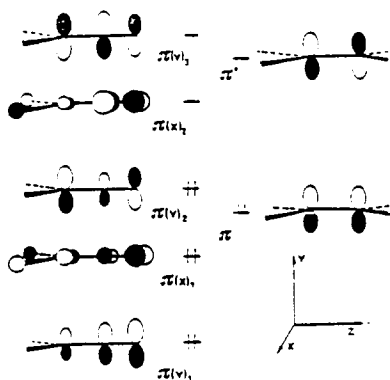
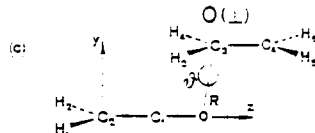
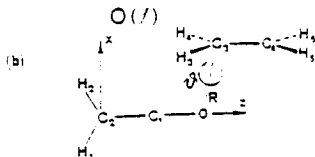
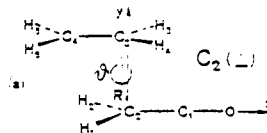


(c) THE APPROACHING DIRECTION IS PERPENDICULAR TO THE PLANE OF KETENE MOLECULE

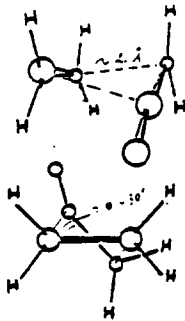


IN BOTH (b) AND (c) CASES THE ETHYLENE MOLECULE CAN ROTATE AROUND THE DIRECTION R. IN THIS WAY ALSO THE POSSIBILITY OF A GAUCHE ATTACK IS TAKEN INTO ACCOUNT.

APPROACHING DIRECTIONS



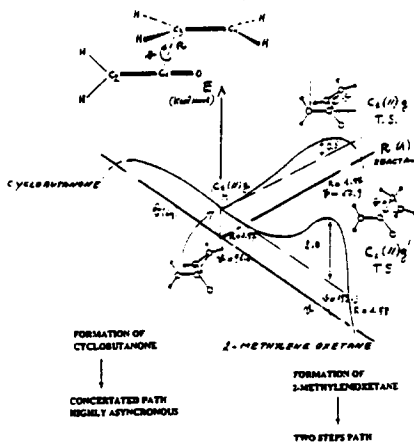
HYPOTHESIS FOR THE STARTING GEOMETRY ASSOCIATED WITH THE SUPRA-ANTARA ATTACK



THEORETICAL CONSIDERATIONS ON THE ELECTRONIC STRUCTURES OF METENE  
THE APPROACH MUST INVOLVE THE TWO H SYSTEMS SIMULTANEOUSLY

THE COMPUTATIONAL EXPERIENCE ON SIMILAR REACTIONS (ETHYLENE - ETHYLENE) CAN SUGGEST REASONABLE STARTING VALUES FOR THE APPROACHING DISTANCE AND THE  $\theta$  ANGLE

PARALLEL APPROACH  $C_{1v}(H)$

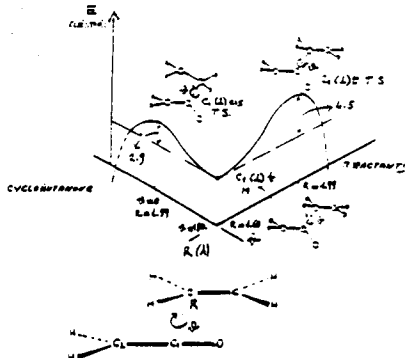


FORMATION OF CYCLOBUTANE  
CONCENTRATED PATH  
HIGHLY ASYNCHRONOUS

1-METHYLENE BUTANE

FORMATION OF 1-METHYLENEBUTANE  
TWO STEPS PATH

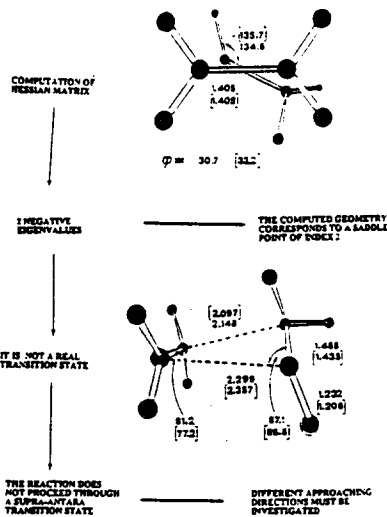
PERPENDICULAR APPROACH  $C_{1v}(H)$



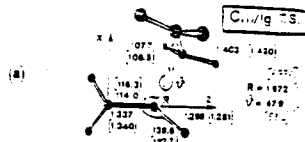
$C_{1v}(H)$  TS AND  $C_{1v}(H)$  TS WITH ALMOST THE SAME ENERGIES

$C_{1v}(H)$  TS ONLY SLIGHTLY DISFAVOURABLE! (-0.5 Kcal/mol)

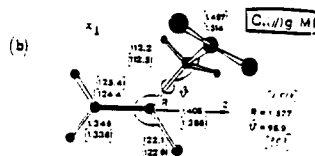
Supra-antara SOSP

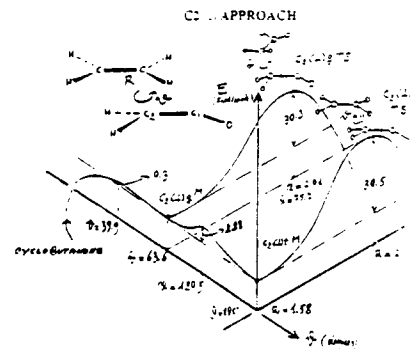
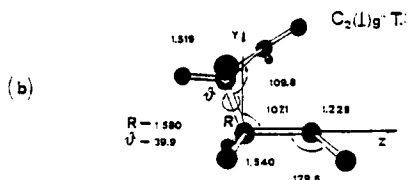
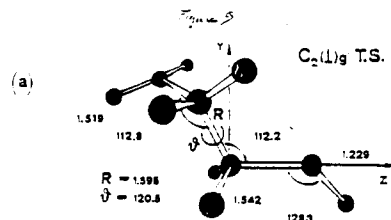
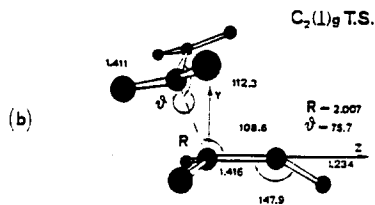
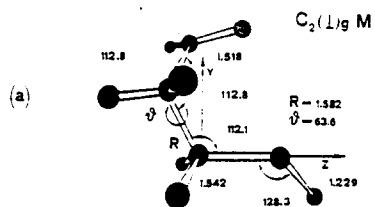
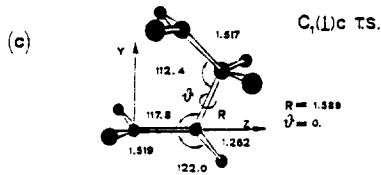
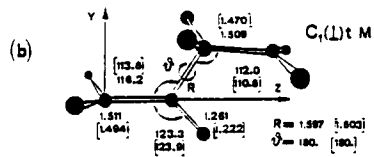
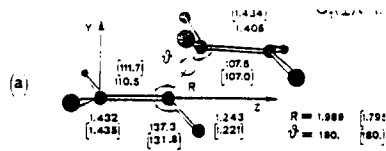


OPTIMUM GEOMETRICAL PARAMETERS OBTAINED FOR THE CRITICAL POINTS ASSOCIATED WITH THE  $C_{1v}(H)$  APPROACH



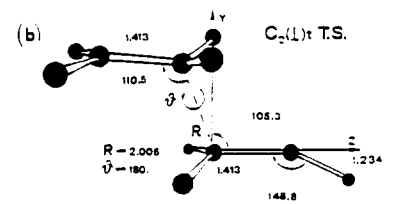
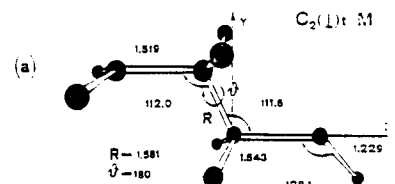
BIRADICAL STRUCTURES

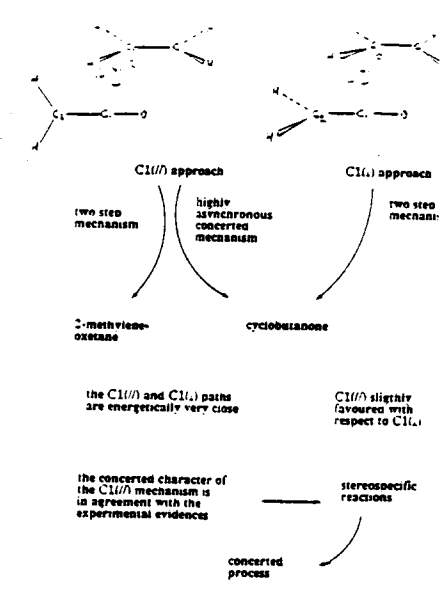
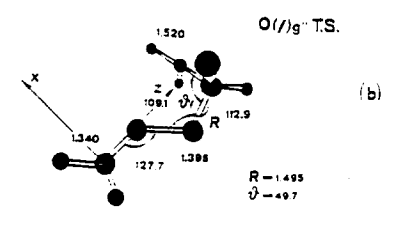
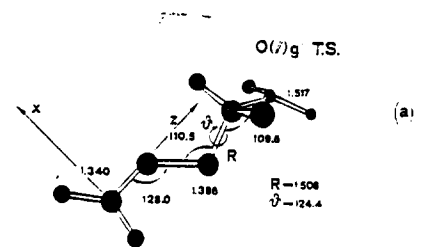
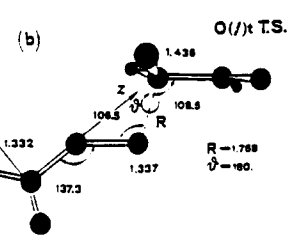
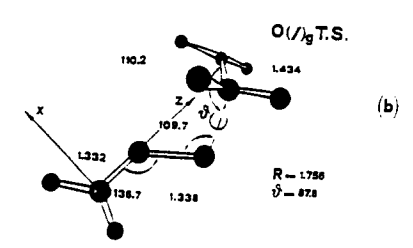
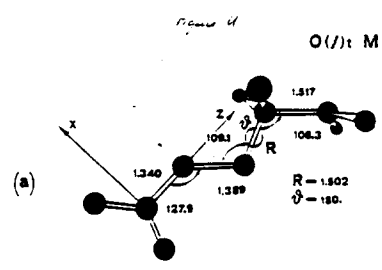
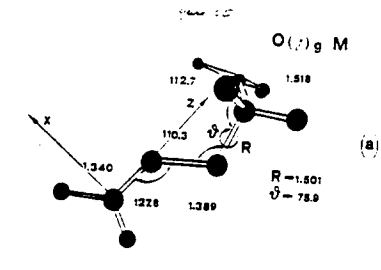
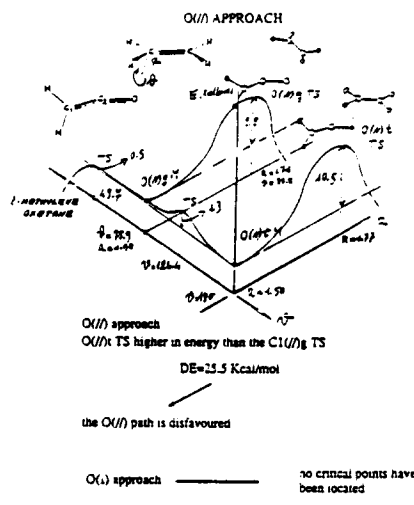


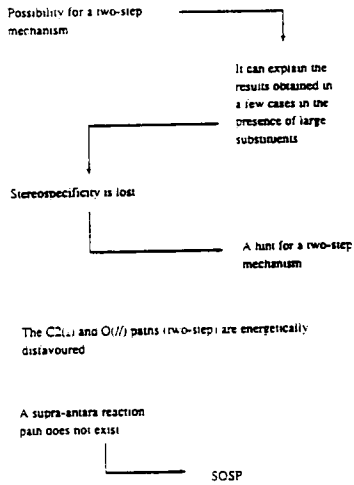


$C_2(I)t$  HIGHER IN ENERGY THAN  $C_1(I)t$  T.S.  
 $DE = 14.8$  kcal/mol.

$C_2(I)t$  DISFAVOURABLE PATH — INVOL HIGHLY ACTIVE ENERGY





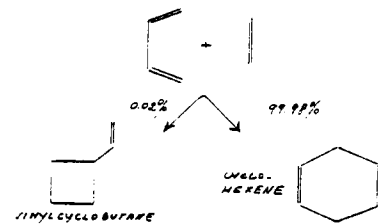


**AN NCSF STUDY OF THE DIELS-ALDER REACTION BETWEEN ETHYLENE AND BUTADIENE**

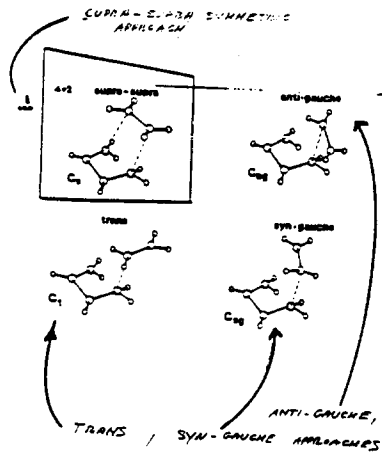
by **BERNARD F. COTTON** and **A. H. EMMETT**  
 Dipartimento di Chimica, G. Galvani  
 dell'Università di Bologna  
 M. A. RICE  
 Department of Chemistry, King's  
 College of London

A LARGE NUMBER OF EXPERIMENTAL AND THEORETICAL STUDIES HAS BEEN PERFORMED ON THIS REACTION

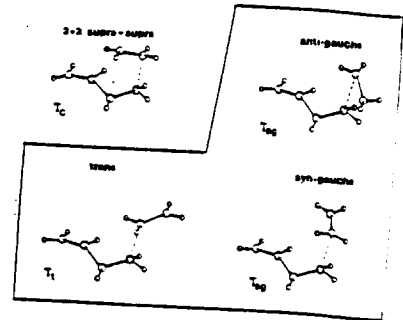
EXPERIMENTAL RESULTS OBTAINED BY **BARTLETT** (1978) SHOW THAT THE PRODUCTS OF THE REACTION ARE:



THE REACTION PATHS WHICH HAVE BEEN INVESTIGATED ARE ASSOCIATED WITH THE FOLLOWING APPROACHES:

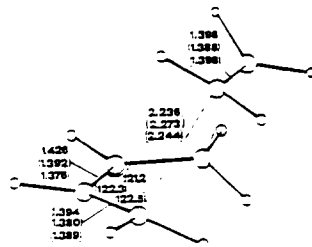


TO UNDERSTAND THE INFLUENCE OF THE STERIC EFFECTS ON THE REACTIVITY OF THE DIENE, THE GAUCHE AND TRANS APPROACHES HAVE BEEN STUDIED ALSO FOR TRANS-BUTADIENE, WHERE THE ONLY PRODUCT CAN BE VINYLCYCLOBUTANE.



Potential Energy Surface for the Attack of Ethylene on Cis Butadiene. Three Critical Points

1) A critical point of  $C_2$  symmetry corresponding to concerted synchronous approach



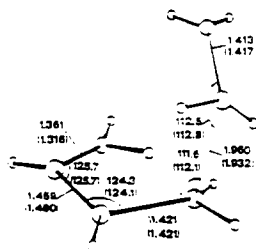
Transition Structure

Hessian matrix with only one negative eigenvalue.

Direction of negative curvature corresponding to approaching distance between the two molecules.



2) A critical point corresponding to a syn-gauche approach (denoted as  $C_{2g}^1$ )



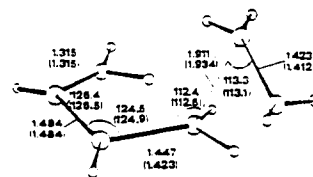
Minimum

Hessian matrix with only positive eigenvalues

This structure lies 2.2 Kcal/mol higher in energy than  $C_2$  transition structure

Closure to cyclohexene without almost any barrier

3) A critical point corresponding to an anti-gauche approach (denoted as  $C_{2g}^2$ )



minimum

Hessian matrix with only positive eigenvalues

This structure lies 5.6 Kcal/mole higher in energy than the  $C_2$  transition structure

Closure to vinyl-cyclobutane involves a transition structure of conformational type with a barrier of 5.2 Kcal/mol.

Attack of Ethylene on Cis Butadiene  
Three different reaction paths

