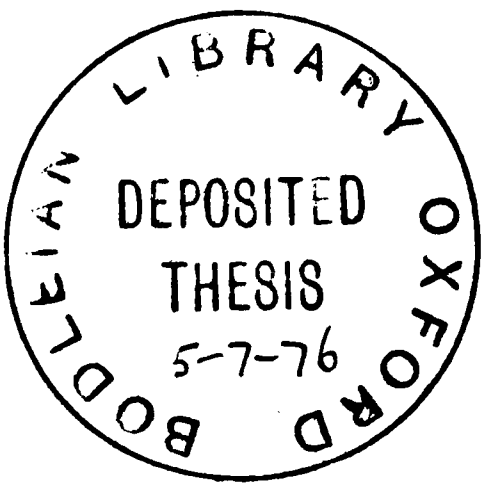
SOME MOLECULAR ORBITAL CALCULATIONS OF THE POTENTIAL SURFACES OF ORGANIC MOLECULES

Abstract of a thesis presented for the degree of D.Phil. in the University of Oxford.

by

L. Clyne



Brasenose College

November 1975.

In this thesis, molecular orbital calculations are used to study a variety of organic reactions, most of which involve molecules containing a large number of atoms. The purpose of the investigation is to elucidate the factors which bring about the stereospecificity found in certain acyclic reactions and to try and relate these factors, if possible, to those that operate in stereospecific pericyclic reactions.

Chapter 1. Molecular Orbital Theory and Organic Reactions.

The application of molecular orbital theory to organic chemistry is a relatively recent phenomenon. One area in particular that has been studied is that class of reactions known as pericyclic reactions. The various concepts and theories that have been used to explain the preferred modes of reactions are reported in this Chapter. The few calculations and simple theories that have been put forward to describe aspects of the complementary field of acyclic reactions are then enunciated. Finally a simple theory based on the use of Hückel molecular orbital theory is proposed, which seeks to explain the known conformational preferences of a large number of acyclic reactions.

Chapter 2. Theoretical Methods.

In this Chapter, a summary of molecular orbital procedures is given, including descriptions of both ab initio and semiempirical methods. The relative advantages and disadvantages of the various approaches are discussed, especially in relation to the type of problems that are involved. The MINDO/2 semiempirical program is described in detail, as is the particular version used (OPTMO) for a large proportion of the work in thesis. Further details of the molecular orbital programs are given in an Appendix.

Chapter 3. Stereospecificity in Organic Reactions.

As a first step in testing the validity of the proposed simple Hückel theory of acyclic reactions, ab initio perturbational calculations are performed on allyl and butadiene species containing varying numbers of electrons. However difficulties are encountered in interpreting the results of the sophisticated calculations and relating them to the simple model. A variety of bonding indices are considered and used. It is decided that the only reliable method of analysis must first partition the total energy into uni- and multicentre terms, in order to discover the precise origin(s) of increased stability in a particular intermediate/transition state(T.S.) A means of carrying this out, within the context of the MINDO approximation, is described.

With this as the basis for investigation, simple models for the S_N2 and S_E2 reactions are studied. It is found that although certain 2-centre energy terms (i.e. bonding terms between 'non-bonded' atoms) stabilise the preferred geometry-optimised intermediate, as predicted by the simple theory, the decisive terms are several 1-centre energy terms. The origin of these terms cannot be explained by the simple theory.

In order to discover how these terms might arise, symmetrical models are examined, with geometries in between those of the two intermediates/T.S.s. These models are distorted by small amounts, towards the two intermediates, and the resulting changes are analysed in terms of perturbation theory. It was observed that inter-molecular orbital mixing is greater for the distortion towards the preferred intermediate and that this increased mixing can account

completely for the difference in the energy changes of the two distortions. This differential mixing is also found to persist in the intermediates themselves. In particular, HOMOπ - LUMOσ* electron transfer is paramount.

Similarly, geometry-optimised models and symmetrical 'intermediate' models are studied for the S_N2' and S_E2' reactions. Again the symmetrical models are distorted towards the final intermediates. Now both HOMOπ - LUMOσ* and, to a lesser extent, HOMOσ - LUMOπ* electron transfer are of decisive importance in the distortions towards the preferred intermediates. (NB. There were no π* orbitals for the previous models). The qualitative magnitude of HOMO-LUMO, σ/π, mixings can be predicted from the symmetrical 'intermediate' models, simply by consideration of the symmetries of the borderline MOs with respect to the symmetry elements maintained during the distortions.

These conclusions provide the basis for the study of a variety of stereospecific reactions. Elimination reactions and the backbone rearrangement are examined using symmetrical 'intermediate' models. In all cases HOMO-LUMO, σ/π, considerations lead to the correct prediction for reaction preference, even when the incoming and leaving groups are not identical. Pericyclic reactions are also considered in the same manner and again the allowed modes of reaction are correctly predicted by HOMO/LUMO considerations.

The dangers of indiscriminate use of simple theories are shown in the study of the 'S_N2 type' reaction of hydroxide ion with ethylene oxide (to give ethylene glycoxide). The energy partitioning method shows that this is <u>not</u> a simple 'S_N2 type reaction' and hence it comes as no surprise to find that HOMO/LUMO considerations are not applicable here. This in fact underlines the inadequacies of the

simple Hückel theory for the explanation and prediction of conformational preference. However it might still be applicable in order to differentiate between configurational isomers. This possibility is briefly examined and ideas for further study in this direction are suggested.

Finally several points of general interest are discussed, including the relevance of calculations on isolated molecules to chemical reactions in solution and the factors which determine the extent of orbital mixing. A simple perturbational model applicable to many acyclic organic reactions is then advanced, which leads to the same predictions and similar explanations as the more detailed calculations had produced. It also has the advantage of being closely related to the previous treatments of pericyclic reactions. The determining factor in both cases is found to be the total number of mobile electrons involved in the 'decisive' parts of the transition states/intermediates.

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Units and Notation.

Two units of length are used:

1 Ångstrom = 10^{-8}cm.

1 atomic unit (Bohr) = 0.52917Å

Similarly, two units of energy are employed:

1 kilocalorie/mole = 4.185 KJ/mole

1 atomic unit (Hartree)/molecule = 627.10 Kcal/mole.

Where no indication is given, the values of lengths and energies are in atomic units. For relative energies, the more stable species has the more negative, or less positive, value.

Xr, Xs, Xu and Xv represent atomic orbitals and ϕ_i, ϕ_j etc. represent molecular orbitals. Ψ is the total wavefunction of a species and subscripts A,B etc. refer to atomic centres in the species. For two-electron integrals, the operator $\frac{1}{r_{12}}$ is assumed, i.e.

$$\langle rs|uv\rangle = \int Xr^*(1)\,Xs(1)\,\frac{1}{r_{12}}\,Xu^*(2)\,Xv(2)\,.\,d\tau_1\,d\tau_2$$

Chapter 1

MOLECULAR ORBITAL THEORY AND ORGANIC REACTIONS.

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General Introduction.

This thesis is concerned with the elucidation of the factors which determine the stereochemistry of a large number of organic reactions. The problem is approached from two directions. Simple theoretical models are set up as a guide to understanding the reaction preferences known to occur. At the same time, ab initio and semiempirical calculations are carried out, in order to test these models at a much higher level of theoretical analysis.

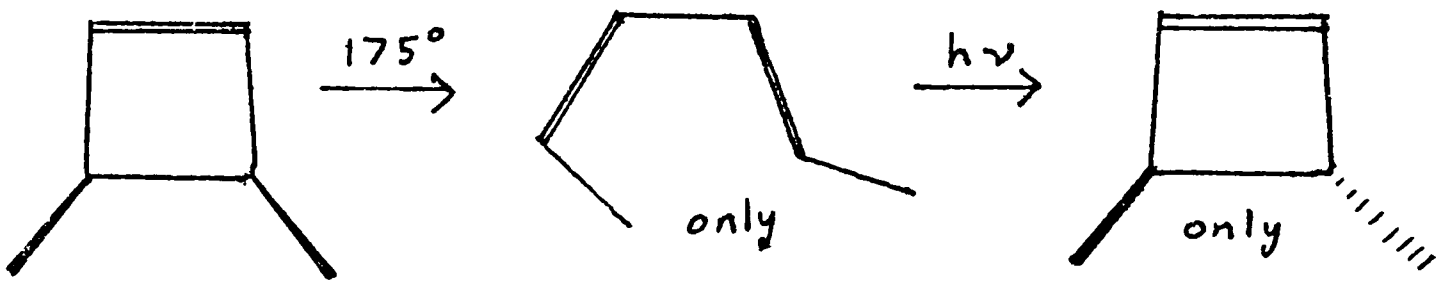
In this introductory chapter, an attempt will be made to review the various previous models and theoretical concepts that have been applied to the reactions under examination, and to related reactions. The few relevant calculations that have been carried out will also be mentioned. Finally the original ideas that initiated this study will be presented, in order to explain the initial direction of the work.

Molecular Orbital Theory and Pericyclic Reactions

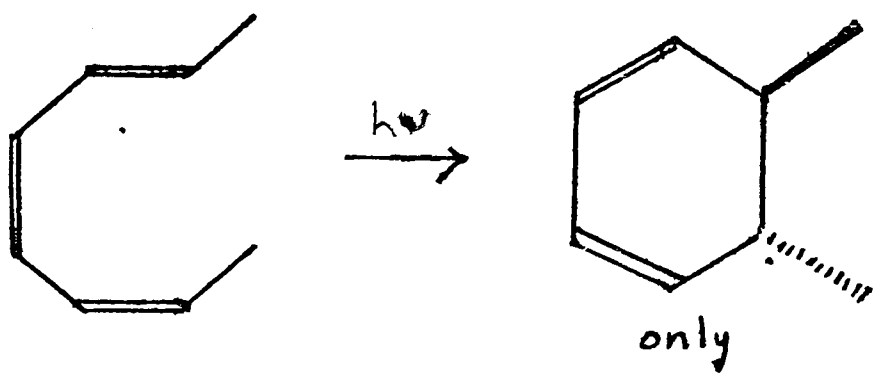
Theoretical analyses of chemical bonding have been applied to a variety of problems in organic chemistry. When used, the molecular orbital method (c.f. Chapter Two) has been particularly successful. However the major part of previous studies has been concerned with the properties of stable ground state molecules, and an investigation of the dynamics of all but the simplest of chemical reactions has been largely ignored. One notable exception has been that class of reaction known as pericyclic reactions.

Pericyclic reactions may be defined as reactions which involve a cyclic transition state, and for which there are no definable intermediates. The three major groups of pericyclic reactions are electrocyclic (ring

Electrocyclic Reactions.

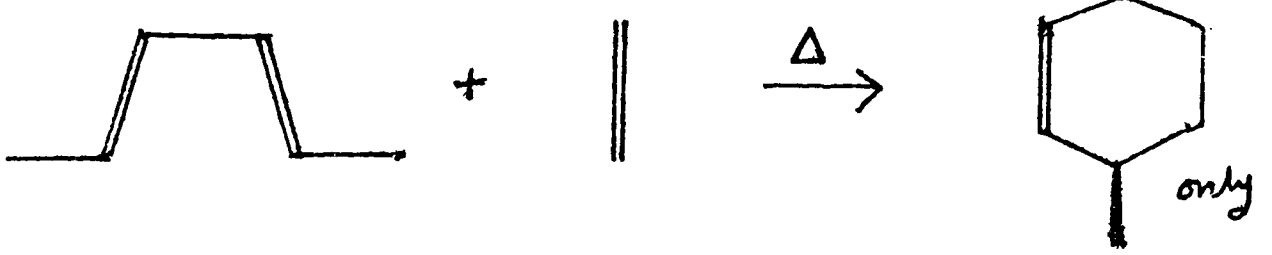


VOGEL (1958)

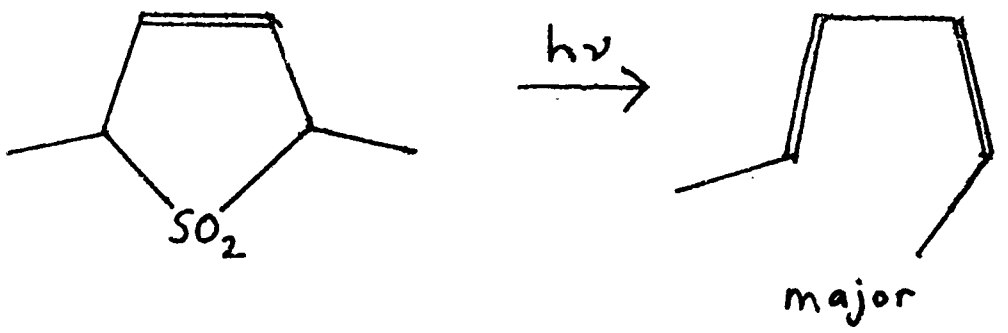


VOGEL et. al. (1965)

Cycloaddition and Cycloelimination.

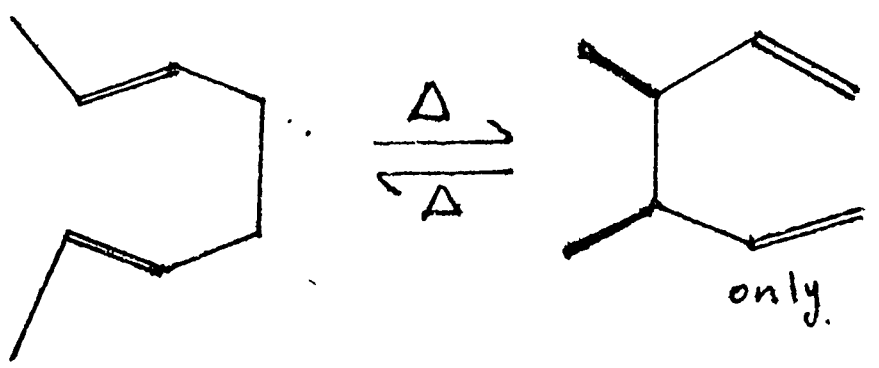


DIELS-ALDER (1928)



+ SO_2 SALTIEL, METTS (1967)

Sigmatropic Reaction.



COPE et. al. (1940)

Figure 1.1. Examples of Pericyclic Reactions

opening and ring closing) reactions, cycloadditions/cycloeliminations and sigmatropic reactions. Examples of these three types are given in Figure 1.1. In all cases, two or more products are possible, but only one is stereospecifically formed. Several attempts have been made to explain these phenomena and it will be instructive, in relation to later discussions, to describe the various approaches.

The first and probably most famous rationalisation is that of Woodward and Hoffmann(1965), which uses the concept of conservation of orbital symmetry. As an example, let us consider the ring closure of butadiene to cyclobutene (Figure 1.2). This process may occur via a conrotatory or disrotatory mode, where this refers to the relative motions of the terminal methylene groups. The Woodward-Hoffmann rules relate the preferred mode of reaction to the number of electrons in the system.

In butadiene, the σ and π orbitals can be separated, as the molecule is planar. This allows one to calculate the forms and relative energies of the π orbitals by the Hückel method (1931). The results of this calculation are shown in Figure 1.3, together with details of the symmetry of these orbitals with respect to (a.) two-fold rotation about the axis shown and (b.) the mirror plane through the same axis, perpendicular to the molecular plane. These symmetry elements are considered because they are the ones maintained respectively, throughout the conrotatory and disrotatory reactions (Note, this assumes that the methylenes rotate by equal angles at all times). The original suggestion was that the highest occupied molecular orbital (HOMO) determined the mode of reaction. The molecular motion should be such that the ends of this orbital overlap in phase. Thus for butadiene, $\emptyset_2$ is the HOMO, and in order to bring about positive overlap a conrotatory mode is predicted, as is found experimentally.

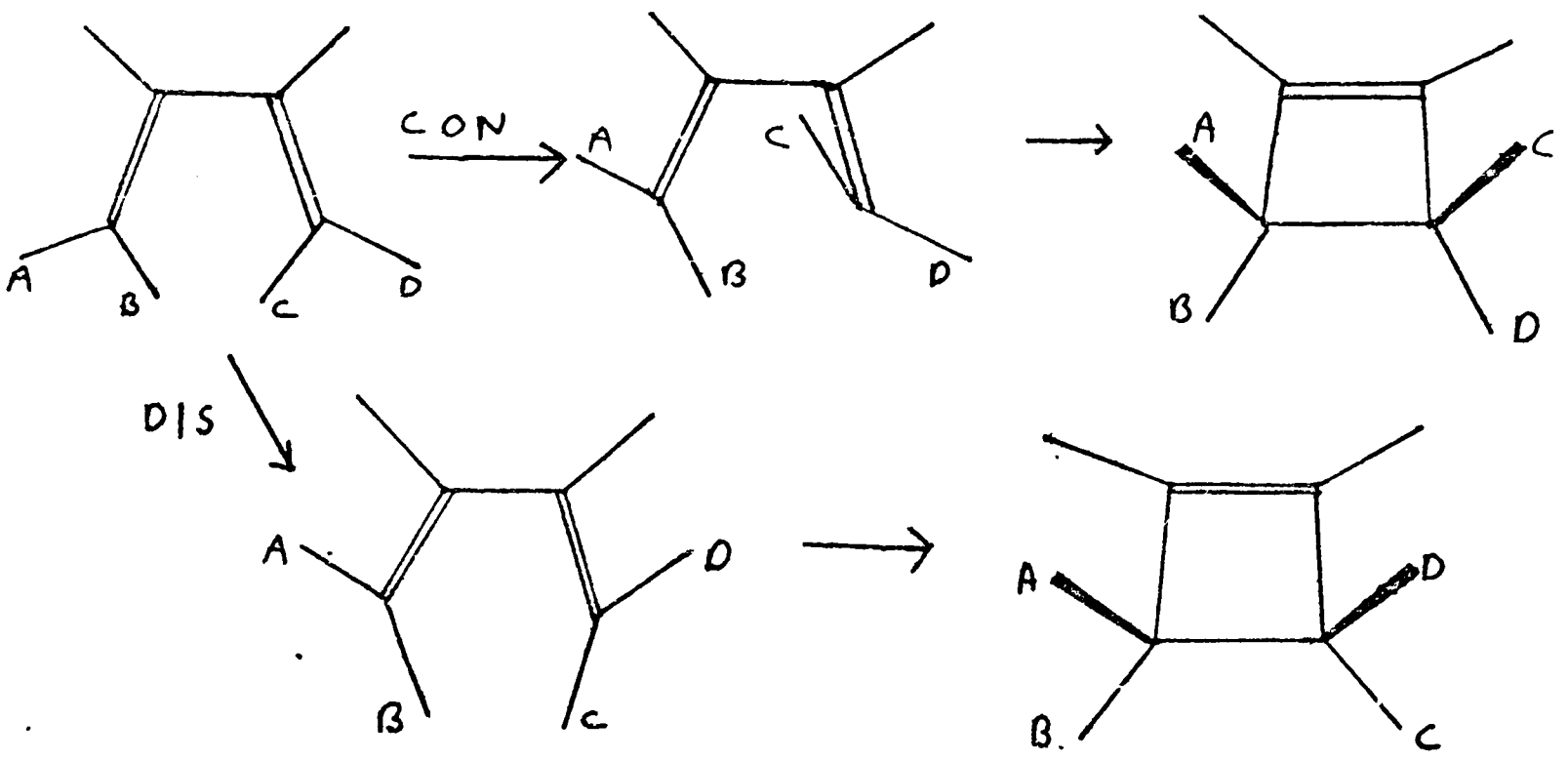


Figure 1.2. The Conrotatory and Disrotatory Interconversions of Butadiene and Cyclobutene.

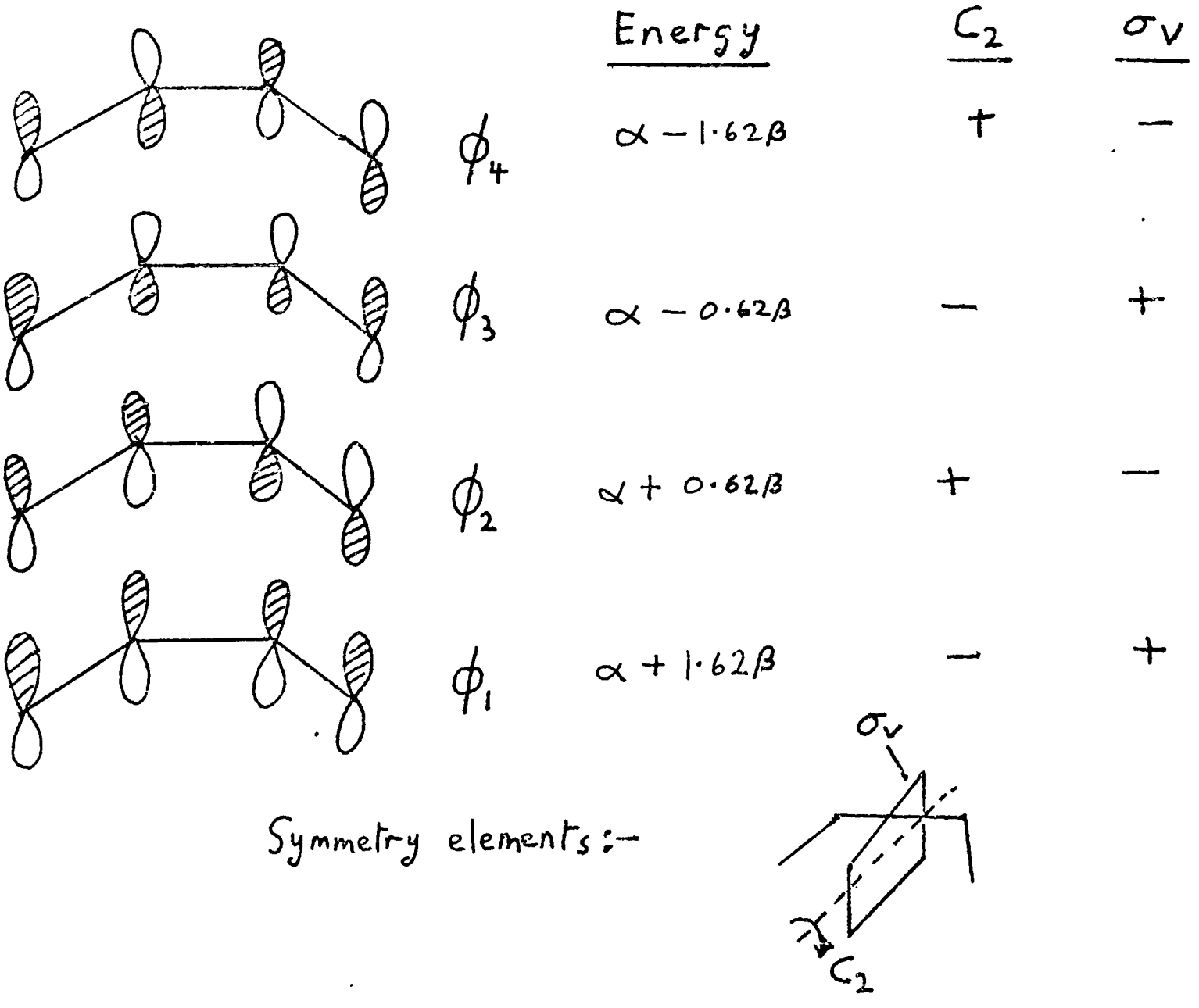
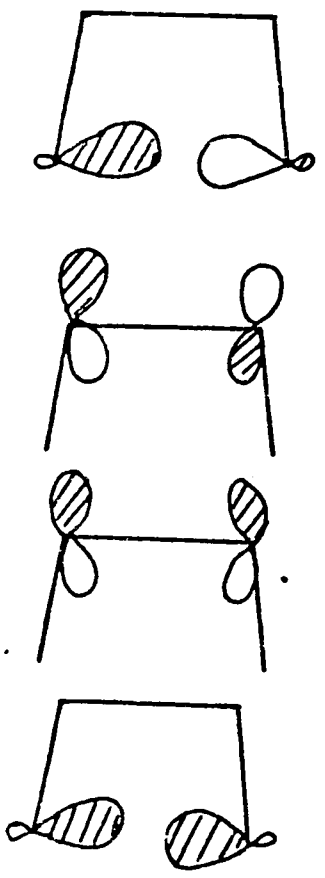


Figure 1.3. The Hückel π- Molecular Orbitals of Butadiene.

This simple approach was later refined by Longuet-Higgins and Abrahamson (1965) to include all 'valence' orbitals. In the example under consideration, this requires analysis of the cyclobutene molecular orbitals as well as those of butadiene. In terms of bonds formed and broken in the reaction, it may be said that the two π bonds of butadiene are 'converted' into a π and σ bond of cyclobutene. Molecular orbitals in the product, representing this change are shown in Figure 1.4. (Note the energy ordering is intuitive, based on the assumption that a σ bond is stronger than a π bond). It can be seen that the number of orbitals which are symmetrical with respect to each symmetry element are the same for both cyclobutene and butadiene. Thus it is possible to construct correlation diagrams which are closed, i.e. all of the reactant orbitals have their counterparts in the product orbitals. This is shown in Figure 1.5. Four electrons must be accommodated in these orbitals. For the disrotatory mode, the ground state configuration of butadiene, $\phi_1^2 \ \phi_2^2$, will be correlated with the doubly excited configuration $\sigma^2 \ \pi^{*2}$ of cyclobutene, i.e. an energetically unfavourable correlation. Whereas for the conrotatory mode, the correlated configuration is $\sigma^2 \ \pi^2$, the ground state of cyclobutene. Thus the thermal reaction is predicted to occur in a conrotatory mode. (Note, in the excited state, ϕ_2 and ϕ_3 each have a single electron and the lowest energy correlation, to $\sigma^2\pi \ \pi^*$, is via the disrotatory mode, which is found to be the preferred mode experimentally).

The above analysis involved orbital correlation. A further refinement, again due to Longuet-Higgins and Abrahamson (1965), introduced the more correct correlation of states and invoked configuration interaction considerations. However the above is still valid and the conclusions are the same. It can therefore be seen that the conservation of orbital symmetry is a powerful method of tackling this and many other



	C_2	σ_v
σ^*	−	−
π^*	+	−
π	−	+
σ	+	+

Figure 1.4. The Orbitals of Cyclobutene.

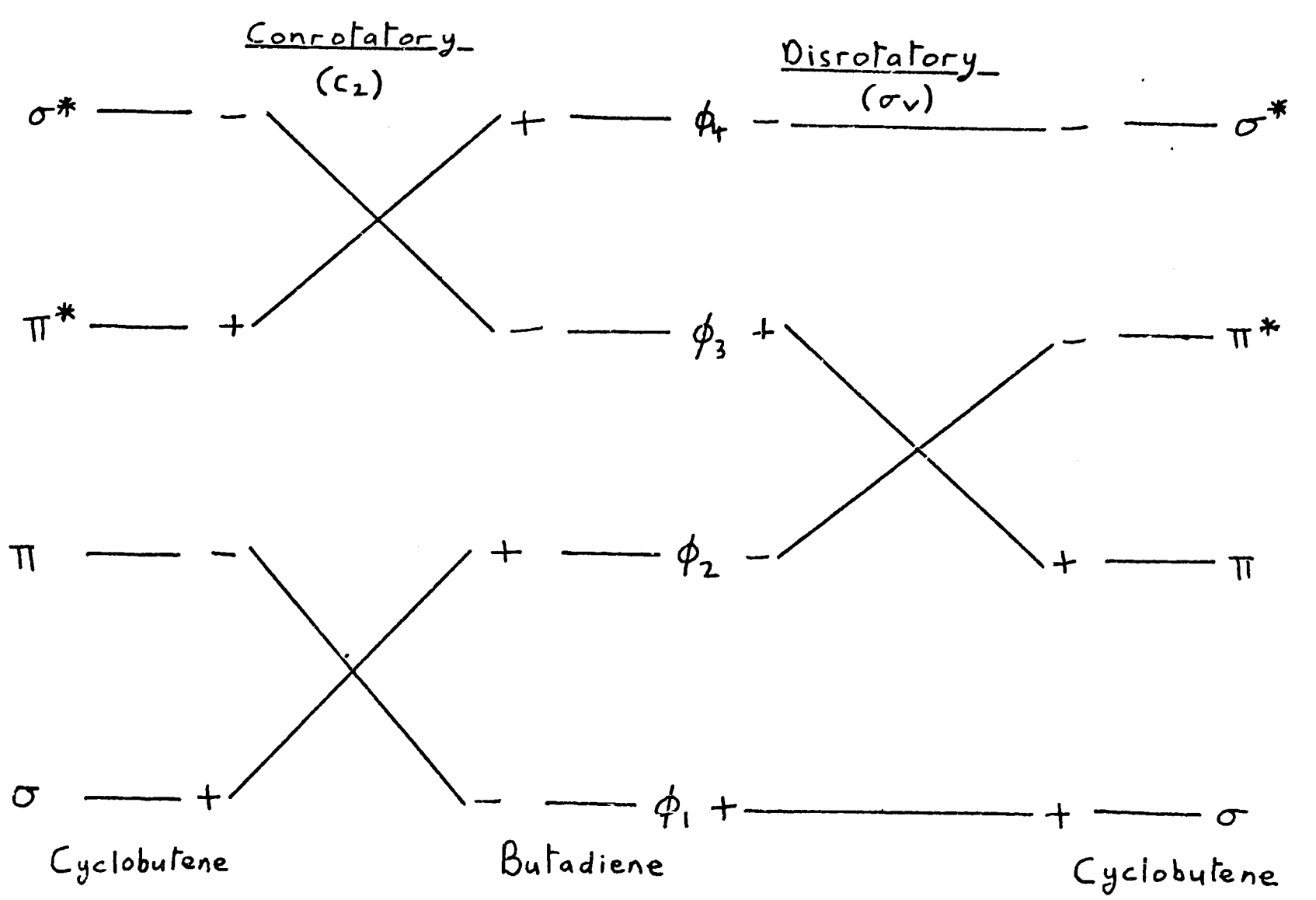


Figure 1.5. Orbital Correlation Diagram for The Interconversions of Butadiene and Cyclobutene.

related reactions. However its very basis, namely symmetry, is also its chief drawback. For any molecule or reaction mechanism not possessing an element of symmetry, this type of analysis cannot be rigorously applied. It was for this reason that other explanations were sought.

A closely related approach, not involving symmetry, was formulated by Fukui (1969, 1971). He had recognised, both from molecular orbital calculations and perturbation theory considerations, the importance of orbital interactions as described above, in rationalising chemical reactions, particularly between the HOMO of a reactant and the LUMO (lowest unoccupied molecular orbital). Although the theoretical basis of his method might not be as sound as that of the Woodwood-Hoffmann treatment, its simplicity and more general applicability make it a very useful tool, especially in its predictive capacity. Its fundamental proposition is as follows:

'A majority of chemical reactions should take place at the position and in the direction of maximum overlapping of the HOMO (or high-lying occupied MO's) and the LUMO (or low-lying unoccupied MO's) of the reacting species; in reacting species possessing a singly occupied (SO) MO, this plays the part of the HOMO or of the LUMO, or of both.'

We shall again use the butadiene-cyclobutene interconversion as our example. The thermal ring opening may be initiated by a mutual charge-transfer interaction between the π bond and the σ bond to be broken. The interactions will take place between the HOMO and LUMO of each bonding region. This is shown in Figure 1.6. It should be noted that as the reaction proceeds, bond stretching and rotation cause the HOMO and LUMO of each region to move closer in energy and hence increase the mutual interactions. The arrows indicate the direction of effective overlapping of HOMO and LUMO and it is concluded that the conrotatory change would be favoured.

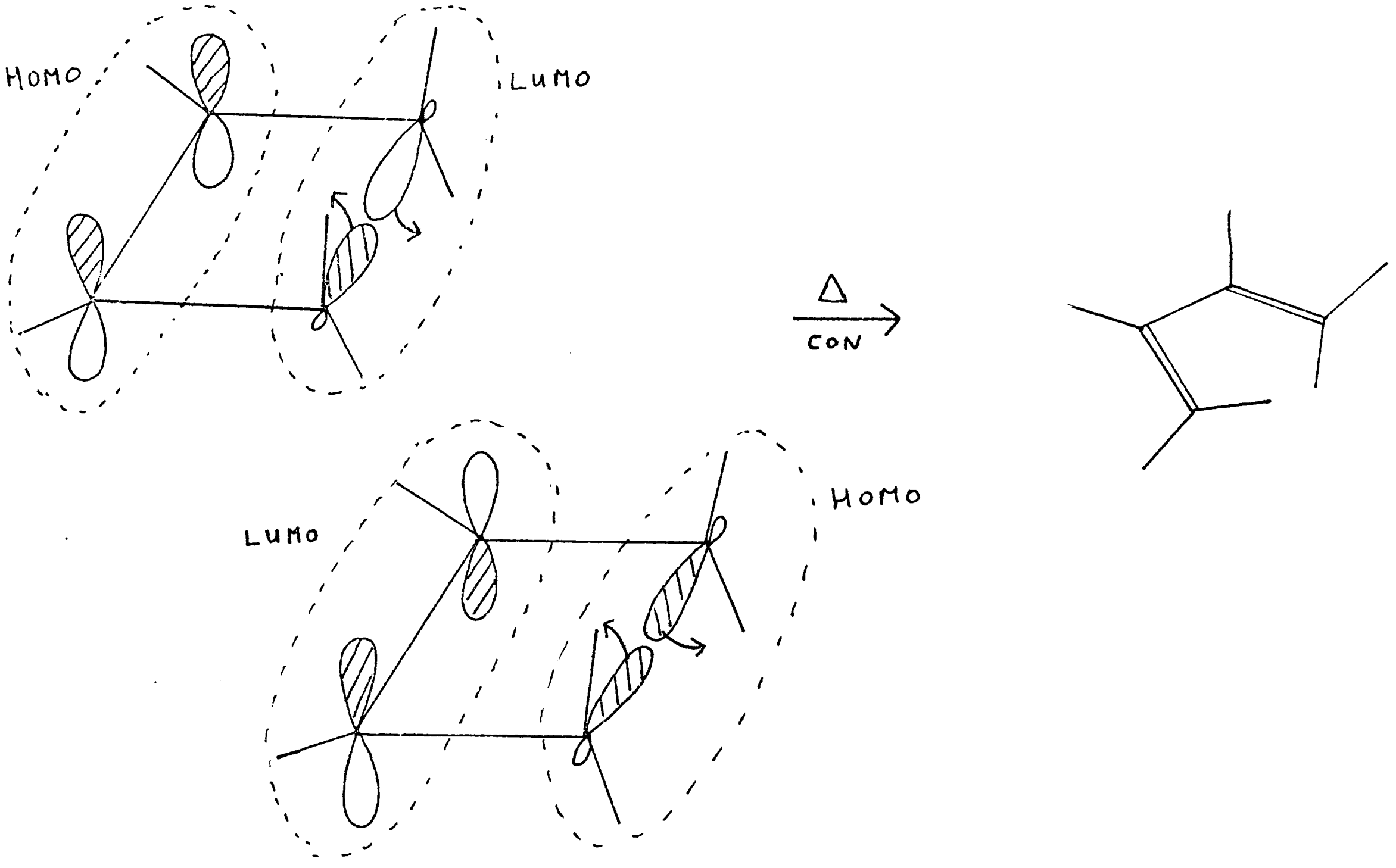
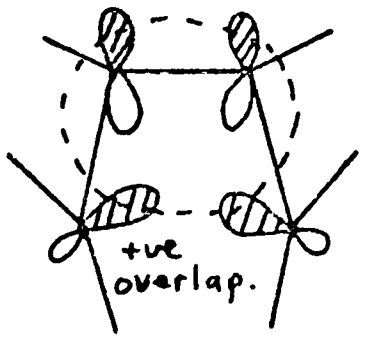


Figure 1.6. HOMO-LUMO Interactions in Cyclobutene.

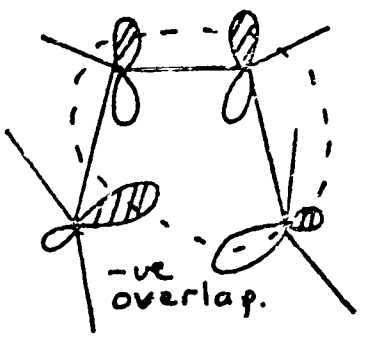
We now have a method which is quick and easy to apply and does not suffer from the restraint of symmetry conservation. However we have moved a step back, in that not all filled 'valence' orbitals are being considered. This is remedied in the approach devised independently, using different formalisms, by Zimmerman (1966, 1971) and Dewar (1971). It is in fact a modern interpretation of the postulate by Evans (1939) that 'concerted cyclic reactions have aromatic transition states.'

The two transition states for the cyclobutene-butadiene conversion are given in Figure 1.7. The four orbitals which are being interconverted are shown and can be used as a basis set to form four molecular orbitals. There is a fundamental difference between the two arrays of orbitals. In the disrotatory transition state there is an even number of sign inversions as one proceeds around the array, whatever the labelling of the lobes (here all are in phase for convenience), whereas the conrotatory transition state must have an odd number of sign inversions. These arrays have been termed Hückel and Möbius respectively. This leads to a radical difference in the energy of the resulting molecular orbitals, which can be seen in the Figure (N.B. The energies are those derived from a Hückel method (1931) calculation, but the qualitative results are independent of this assumption). The Möbius array is 'aromatic' with respect to butadiene and the Hückel array is 'antiaromatic.' In fact butadiene, the reactant, is obviously the most stable, as other σ bond interactions are not considered, but the relative ordering of the two transition states still applies. Table 1.1 gives the generalisation of this analysis, where the number of electrons is the sum of those that are involved in the bond rearrangements.

We now have an explanation which is both of general applicability and treats all 'valence' electrons. Two final related points may be noted. Firstly, if geometrical restraints are imposed, such that a



Hückel array.
(DIS)



Möbius array.
(CON)

Butadiene array.

-2β

-1.62β

-1.41β

-0.62β

α 0β α

0.62β

1.41β

1.62β

2β

Total Energies of the Four electrons

$4\alpha + 4\beta$ $\quad 4\alpha + 4.48\beta$ $\quad 4\alpha + 5.64\beta$

Figure 1.7. Hückel and Möbius Arrays.

Number of Electrons.	Hückel Array	Möbius Array
$4N + 2$	'Aromatic'	'Antiaromatic'
$4N$	'Antiaromatic'	'Aromatic'

Table 1.1. Energetics of Hückel and Möbius Systems.

molecule cannot proceed via the aromatic transition state, a non-symmetric transition state may be attained (Figure 1.8), which involves a non-aromatic array, topologically equivalent to the acyclic polyene. Recent calculations by Dewar (1974), using MINDO/3, indicate the possibility of such a process and thus, if correct, negate the quantitative results of almost all previous work on this and related forbidden reactions, where an element of symmetry had been assumed. A second point however, also raised by Dewar (1974a) in his latest analysis, somewhat tempers this harsh criticism. He shows that symmetry considerations, and calculations based thereon, will always give the correct qualitative answer, even if the actual reaction pathway followed is not the one assumed. Thus although the symmetry concept is of invaluable help to the theoretical organic chemist, if used too readily, it can lead to assumptions which prejudge the conclusions.

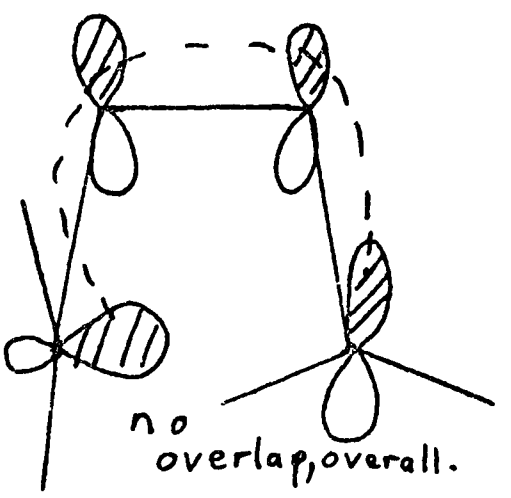


Figure 1.8. An Example of a Non-Aromatic Array.

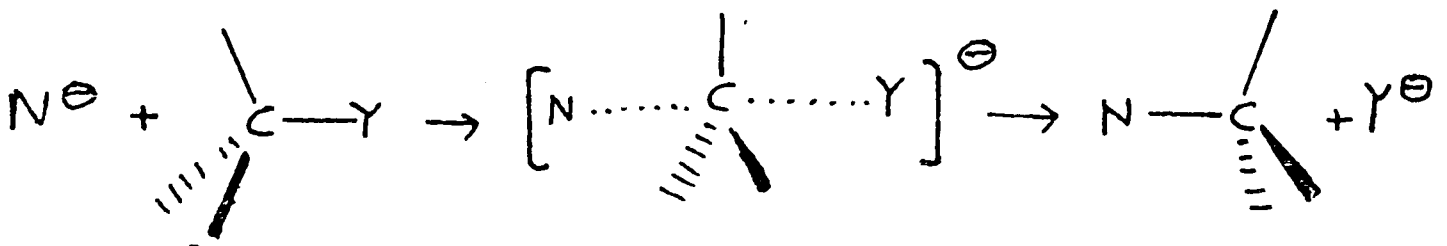
Molecular Orbital Theory and Acyclic Reactions

As we have seen, pericyclic reactions are a subject of great interest to theoretical chemists. This may be attributed to their virtually total stereospecificity, which intrigued early workers. However, even in the realm of acyclic chemistry, there are a large number of reactions which show strong, if not total, stereospecificity. A selection of such reactions is given in Figure 1.9. As can be seen, there is a variety of reaction types represented. Nevertheless, it should be recalled that the different groups of pericyclic reactions also appear superficially to be unconnected.

When one considers previous work in this field, it seems appropriate to divide the results and analyses into two separate categories. There are, on the one hand, those workers who have carried out mainly semi-empirical calculations on reaction pathways, using simple but chemically realistic species as their reactants. Fukui and Dewar are probably the foremost examples of workers using this approach. On the other hand, many researchers use the more fundamental (but not necessarily more chemically accurate) ab initio calculations. However these require much more computer time and hence simplified models and simplifying assumptions are often necessary. Pople and coworkers typify this latter approach.

To some extent this leads to a difference of emphasis in interpretation of the results. In general, it may be said that Fukui et. al. try to derive general theories from the various related studies which they undertake, whereas Pople et.al. are more concerned with the particular system being considered and tend to treat each case separately. It is obvious that both approaches are valid and each has its own merits. Only time will decide which is the more productive.

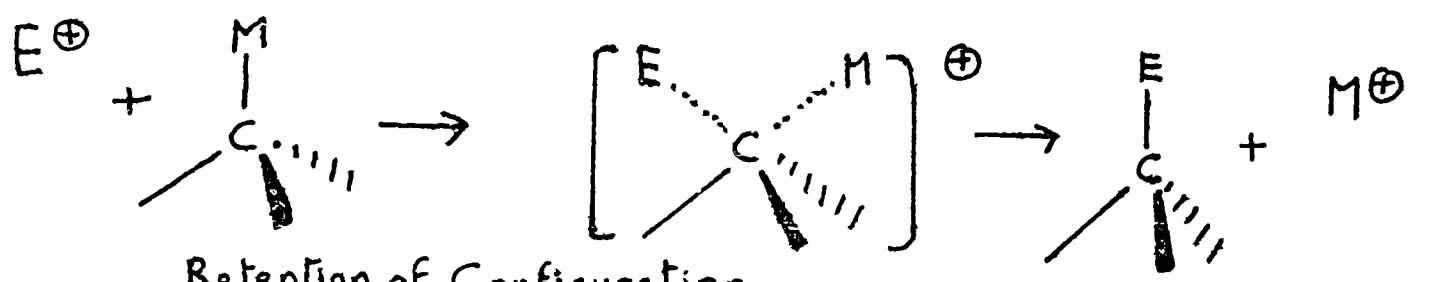
S_N2



Inversion of Configuration.

INGOLD, HUGHES (1935)

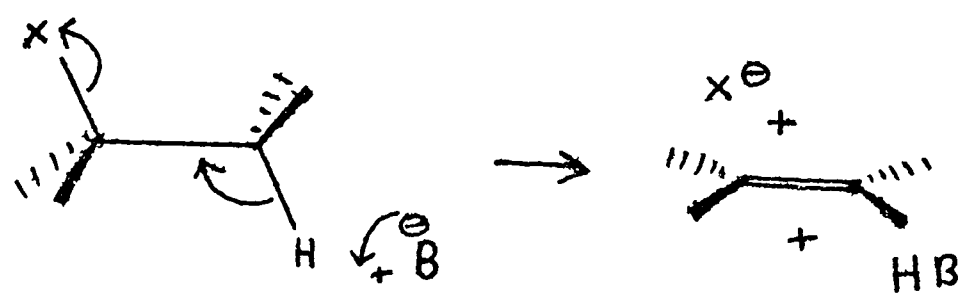
S_E2



Retention of Configuration.

HUGHES et. al. (1959)

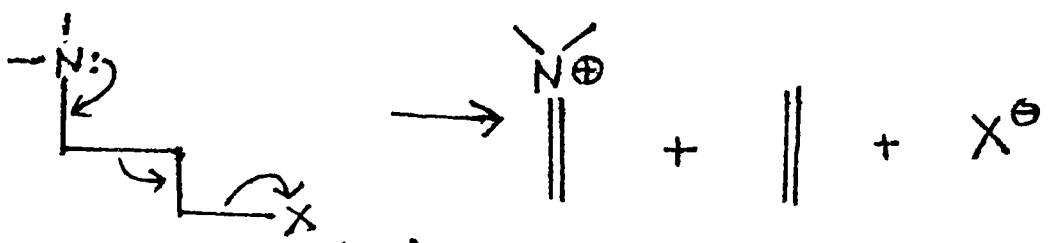
E2



Trans Elimination.

INGOLD, HANHART (1927)

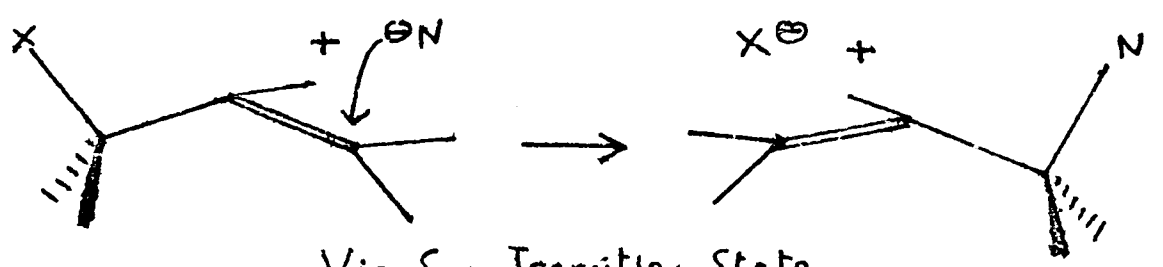
Fragmentation.



GROB (1955)

'W' Conformation.

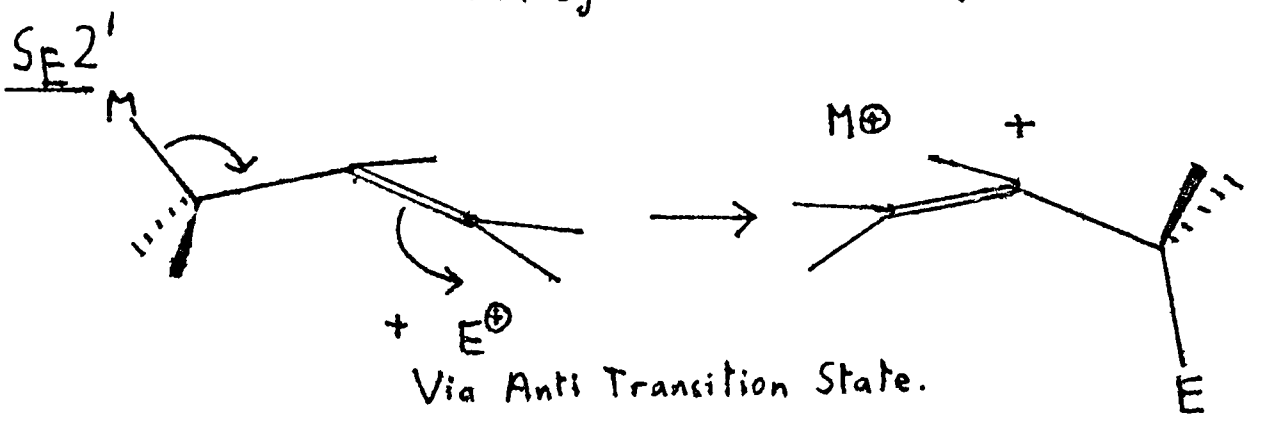
S_N2'



Via Syn Transition State.

STORK, WHITE (1953)

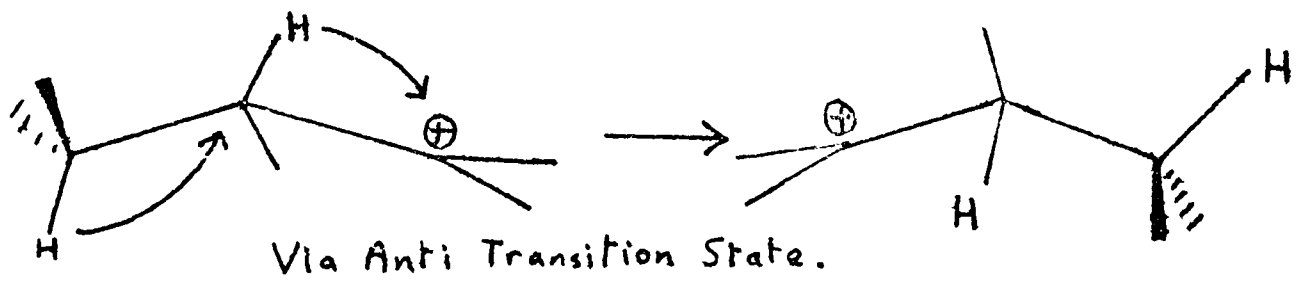
S_E2'



Via Anti Transition State.

FELKIN, FRAJERMAN (1970)

Backbone Rearrangement. (in Steroid Biosynthesis).



Via Anti Transition State.

COREY, URSPRUNG (1955)

Figure 1.9. Stereospecific Acyclic Reactions.

Examples of the ab initio 'school', which are also related to the work in thesis, are given by the studies made on the species $CH_5^{\oplus}$ and $CH_5^{\ominus}$. These ions, of which the former has been experimentally observed by Olah (1968) and Hogeveen (1968,1969), were considered to be suitable models for the S_N2 and S_E2 reactions:

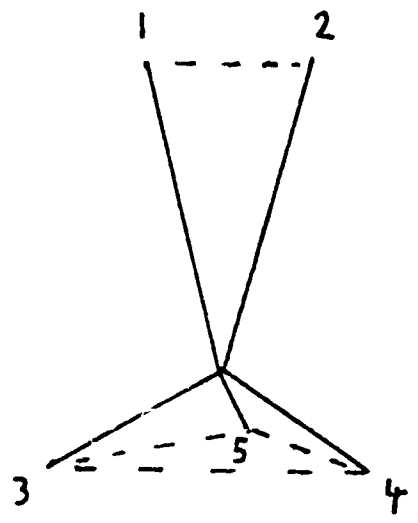
$$S_N2 :- \quad H^{\ominus} + CH_4 \rightarrow CH_5^{\ominus} \rightarrow CH_4 + H^{\ominus}$$

$$S_E2 :- \quad H^{\oplus} + CH_4 \rightleftharpoons CH_5^{\oplus}$$

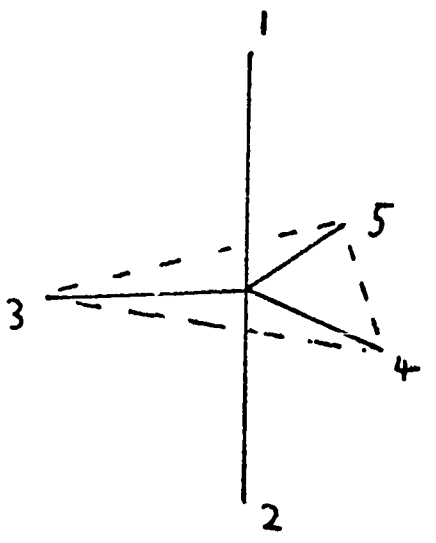
Pople (1972) and Dyczmons (1970) have investigated $CH_5^{\oplus}$ using very large basis sets, while Mulder (1970) and Van der Lugt (1969) have carried out calculations on both systems. In most cases, three symmetries were considered for the species, namely C_s, D_{3h} and C_{4v} (see Figure 1.10). In each case the geometrical parameters were varied independently, several times if necessary, to give the lowest total energy.

All authors, with the exception of Mulder, predicted that $CH_5^{\oplus}$ would be most stable as a species possessing C_s symmetry. On closer examination, it was found that the distance between the carbon and hydrogens 1 and 2 was quite long and that the majority of the charge resided on the carbon and hydrogens 3,4 and 5. It was suggested therefore that a better representation of $CH_5^{\oplus}$ is as a loose complex between $CH_3^{\oplus}$ and H_2. This was further confirmed by calculations which showed that there was no energy barrier to rotation of H_1-H_2. (Note these results have been recently confirmed by Dewar (1975) using MINDO/3. However the details of these calculations will be left until later where they will be of more relevance).

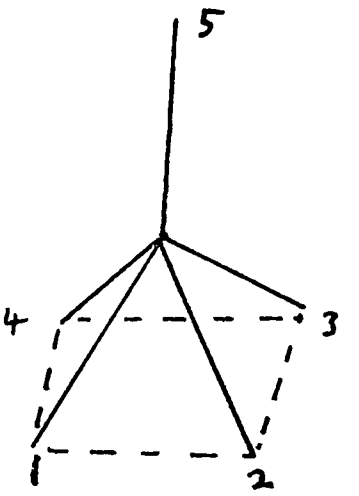
$CH_5^{\ominus}$ on the other hand is definitely not of C_s symmetry and the calculations point to D_{3h} symmetry. Thus if one considers H_1 and H_2, the equivalent hydrogens, as the incoming and departing groups during the course of reaction, one observes that $CH_5^{\oplus}$ ($\cong S_E2$) should lead to



C_s



D_{3h}



C_{4v}

$CH_5^{\oplus}$

Pople (1972).	0·0	16·0	—
Dyczmons (1970).	0·0	14·5	7·8
Mulder (1970).	2·5	3·1	0·0
Van der Lugt (1969).	0·0	3·5	0·3

$CH_5^{\ominus}$

Mulder (1970).	54·5	0·0	54·5
Van der Lugt (1969).	56·8	0·0	54·3

Figure 1.10. Relative Energies, in Kilocalories, of Various Conformations of $CH_5^{\oplus}$ and $CH_5^{\ominus}$.

retention and $CH_5^{\ominus}$ ($\equiv S_N2$) should lead to inversion, which is found experimentally.

The qualitative explanation given was as follows. For $CH_5^{\oplus}$, the D_{3h} structure contains a planar $CH_3^{\oplus}$ group (favourable) and a linear 3-centre bond containing two electrons (unfavourable). The C_s structure contains a pyramidal $CH_3^{\oplus}$ group (unfavourable) and a triangular 3-centre, 2-electron bond (strongly favourable). Thus although there is some cancelling of effects, the C_s structure is preferred. For $CH_5^{\ominus}$ however, the D_{3h} structure has a planar $CH_3^{\oplus}$ group (favourable) and a linear 3-centre, 4-electron system (favourable), whereas the C_s species is unfavourable in both respects. The D_{3h} is now strongly preferred. (In both examples, the C_{4v} conformation is an intermediate case). The simple theory and the elaborate calculations are therefore united in predicting the correct modes of reaction.

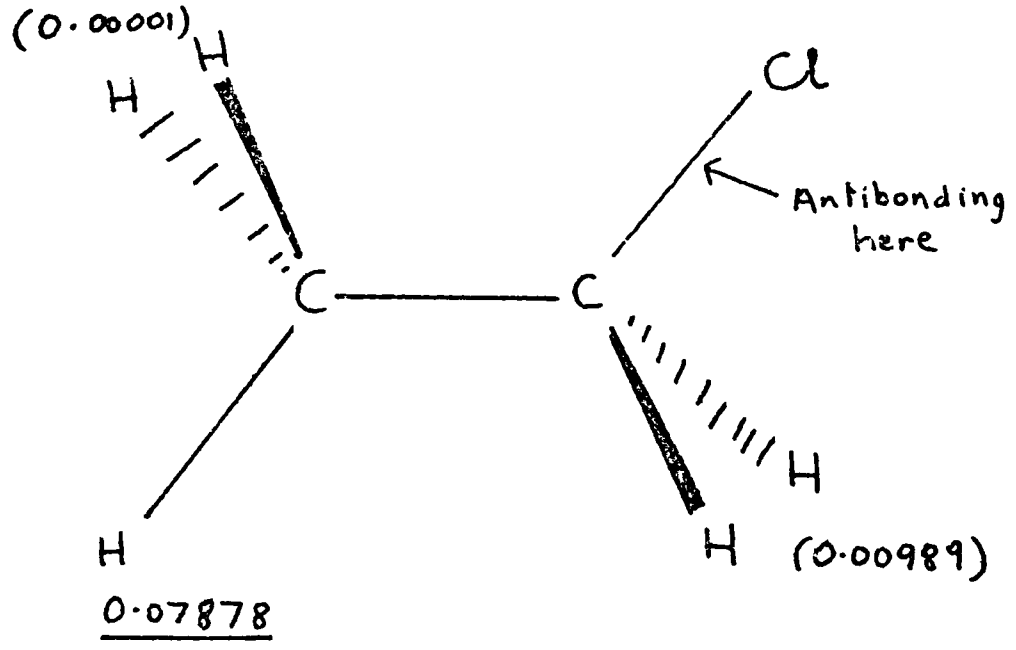
The stimulating article by McIver (1974) might be mentioned in this context. It, in part, concerns the use of group theory in eliminating certain symmetrical atomic configurations as possible transition states. For example, he shows that C_{4v} cannot be the transition state for the S_N2 inversion of CH_4, i.e. $CH_5^{\ominus}$ cannot be most stable as a C_{4v} structure. At the same time one must remember Dewar's warning, already mentioned, of the danger of imposing geometrical restraints on reaction pathways in general, and transition states in particular.

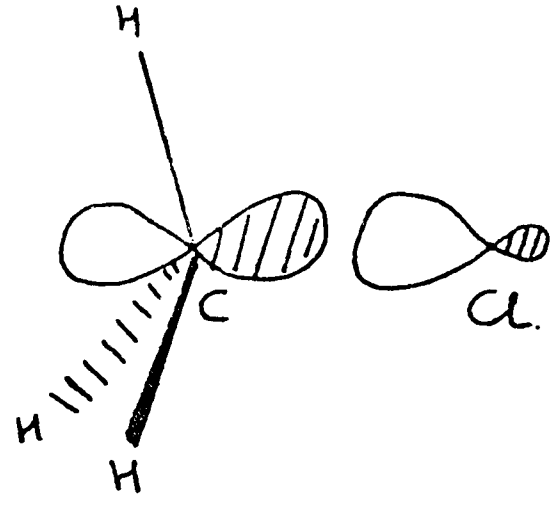
Before leaving this area, mention must also be made of the detailed ab initio studies of Dedieu and Veillard (1972) on the S_N2 reactions of hydride ion and fluoride ion with methane and methyl fluoride. Although they assumed symmetrical rear attack of the nucleophile, all other parameters were varied at points along the reaction pathway. The overall results are in agreement with the qualitative picture already given.

We will now consider the studies of Fukui, who possibly best exemplifies the semiempirical 'school'. His research and theories in this area began with his famous frontier orbital theory of the fifties (1952,1954), in which he showed that the electron densities of the frontier (i.e. HOMO and LUMO) π orbitals in aromatic hydrocarbons can be used to predict the position of attack during reaction. This was later extended to saturated systems, by the use of the Extended Hückel theory method of Hoffmann (1963). Among the reactions which were considered were the S_N2 (1965) and the E2 (1965a).

In both cases an electron donating species attacks the halogenoalkane and hence the electron populations in the LUMO must be considered. If there is a choice possible for the atom to be attacked, the one with the highest electron density in the LUMO, i.e. the one most ready to accept electrons, will be preferred. For example, in the case of elimination of hydrogen chloride from ethyl chloride, the incoming base must remove a proton. In Figure 1.11, the electron populations of the LUMO of ethyl chloride are given and it can be seen that the electron density of the hydrogen trans to the chlorine atom is the greatest. It is therefore predicted that trans elimination is preferred, as is found experimentally. The LUMO of methyl chloride consists mainly of a carbon 2p atomic orbital and a 3p+3s chlorine hybrid orbital pointing at each other, but with a node between them (see Figure 1.11). Attack at the carbon orbital will lead to inversion and at the same time the carbon-chlorine bond will be weakened.

One drawback with the above approach is that only the reactant is considered and not the reaction itself. Also in most cases only one of several reactants are investigated. A more satisfactory plan is obviously to study the reaction pathway or at least some part of it. In more





Ethyl Chloride

Methyl Chloride

Figure 1.11. The LUMO's of Two Halogenoalkanes.

recent studies, Fukui (1968,1969 ,1971a) has done just this, but in a unique way. In order to consider the initial stages of a reaction (i.e. a perturbational approach), he has taken the wave functions of the isolated reactant moleculesand calculated the elements of their interaction energy at varying intermolecular distances, using a C.I. procedure. The four components of this interaction energy he has termed the Coulomb, exchange, charge transfer (delocalisation) and polarisation energies. He has shown that the inclusion of charge transfer was of great importance in explaining the formation of new bonds and the weakening of old bonds as reaction proceeds. The role of HOMO-LUMO interactions was again found to be decisive, as in his previously described treatment of pericyclic reactions, the most important being between the HOMO of the electron donating species and the LUMO of the electron accepting species.

A recent example of Fukui's work (1972), related to the work in thesis, is that of the ring opening of ethylene oxide by hydride ion, which is known to proceed with inversion at the carbon attacked, (Gould (1959)). The semiempirical S.C.F. calculations predicted such an attack and are shown to be directly related to charge transfer terms, in particular between the HOMO of the hydride ion and the two LUMO's of ethylene oxide. Fukui, however, mentions that on deforming the ethylene oxide molecule in order to take account of the presence of the hydride ion, huge changes in the relative energy levels of the molecular orbitals occur. He notes that this casts some doubt on the validity of applying the isolated molecule approach to anything but the very first stages of a reaction. The ideal method would therefore appear to be one which treats the whole system and allows deformation to the lowest total energy as the reaction proceeds, while at the same time being economical enough in computer time to allow the investigation of chemically significant species. A method, based on Dewar's MINDO program and employing

energy minimisation techniques, goes a long way to fulfilling these requirements and has been used for most of the work in thesis. It will be described in detail in the relevant chapter.

If the previous discussion is the acyclic analogue of Fukui's treatment of pericyclic reactions, then we may consider Hoffmann's (1971) analysis of the interactions of localised orbitals as the acyclic analogue of his symmetry treatment of pericyclic reactions. Hoffmann recognised two ways in which localised orbitals can interact and hence stabilise or destabilise a species. He called these types of interactions 'through space' and 'through bond'. They may be, and usually are, both present to varying degrees, sometimes reinforcing one another and sometimes counteracting each other. As an example of the latter, let us consider the 1,4-cyclohexene biradical. This may be written as shown (Figure 1.12(b)) with the two localised orbitals each containing an unpaired electron. Assuming no interaction the symmetric (A+B) and antisymmetric (A-B) combinations will be of equal energy.

On increasing the direct through space coupling (1.12(a)), by bringing the two centres together, it can be seen that the symmetric bonding combination will become the lower energy combination. Thus the HOMO will be symmetric.

However the two orbitals interact in another way via the intervening σ bonds; and when the two centres A and B are far apart, this 'through bond' coupling is the dominant one. We shall consider the coupling via the two central σ bonds, as these are the only uniquely located bonds (the other σ bonds appear as pairs of symmetry related bonds and to a first approximation their effects on the orbitals in question will cancel out). Now we can classify the relevant orbitals according to the symmetry plane (Figure 1.13). On mixing orbitals of like symmetry the lower orbital is stabilised and the higher orbital destablised. The

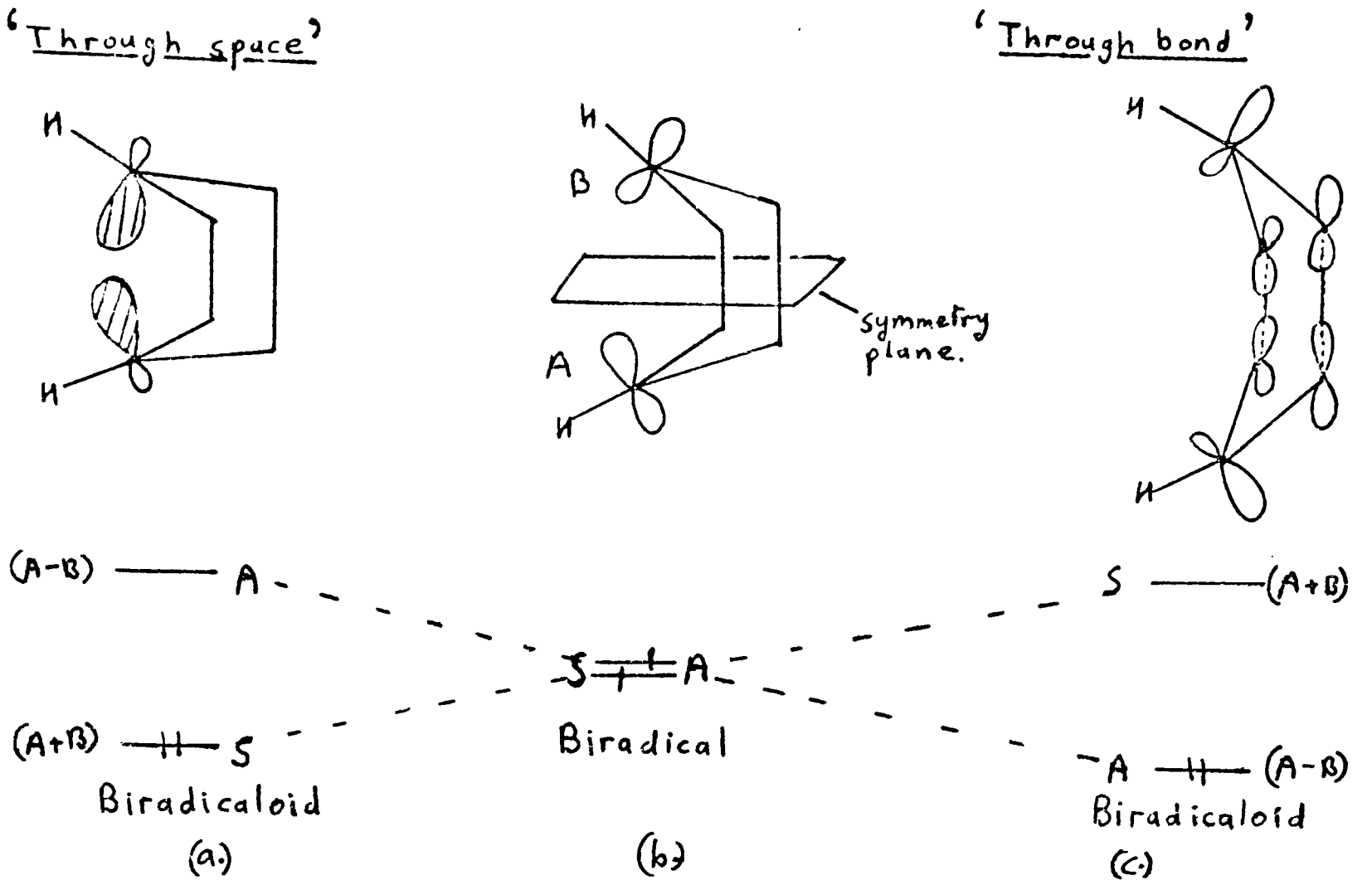


Figure 1.12. Through Space and Through Bond Coupling in 1,4 - Cyclohexene Biradical.

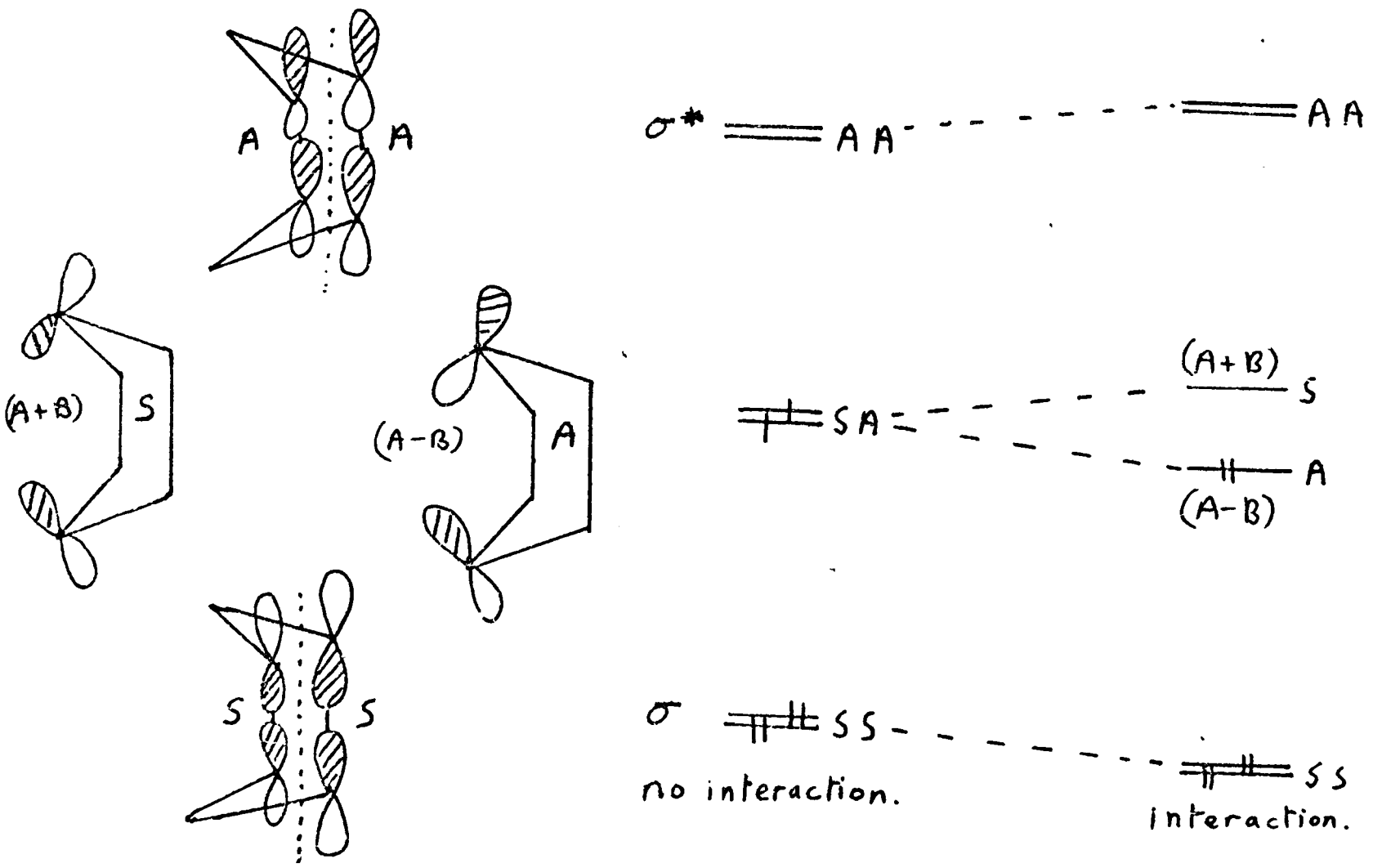


Figure 1.13. Through Bond Interaction.

results can be seen and now the antisymmetric combination (A-B) is of lower energy and hence the HOMO.

Therefore depending on the relative strengths of these two effects, one can produce two totally different species. Dewar (1974a) has termed such a pair of species lumomers, as a HOMO-LUMO crossing is involved on going from one to the other, (via the biradical). This is not just a theoretical distinction, for in the 'boat' Cope rearrangement centres A and B are distant and a 'through bond' biradicaloid is the intermediate, whereas in the inversion of bicyclo-2,2,0-hexane the centres A and B are near and a 'through space' biradicaloid is the intermediate (Figure 1.14). These reactions therefore do not involve a common intermediate and leakage from one to the other is barred by the biradical barrier separating the two species.

It can be seen therefore that several theories of varying complexity have been put forward to explain the known stereochemical preferences in acyclic chemistry. However at present insufficient detailed and accurate calculations have been performed to show that one particular theory is superior to the rest. It is to be hoped the work described here will go a little way to bridging this gap.

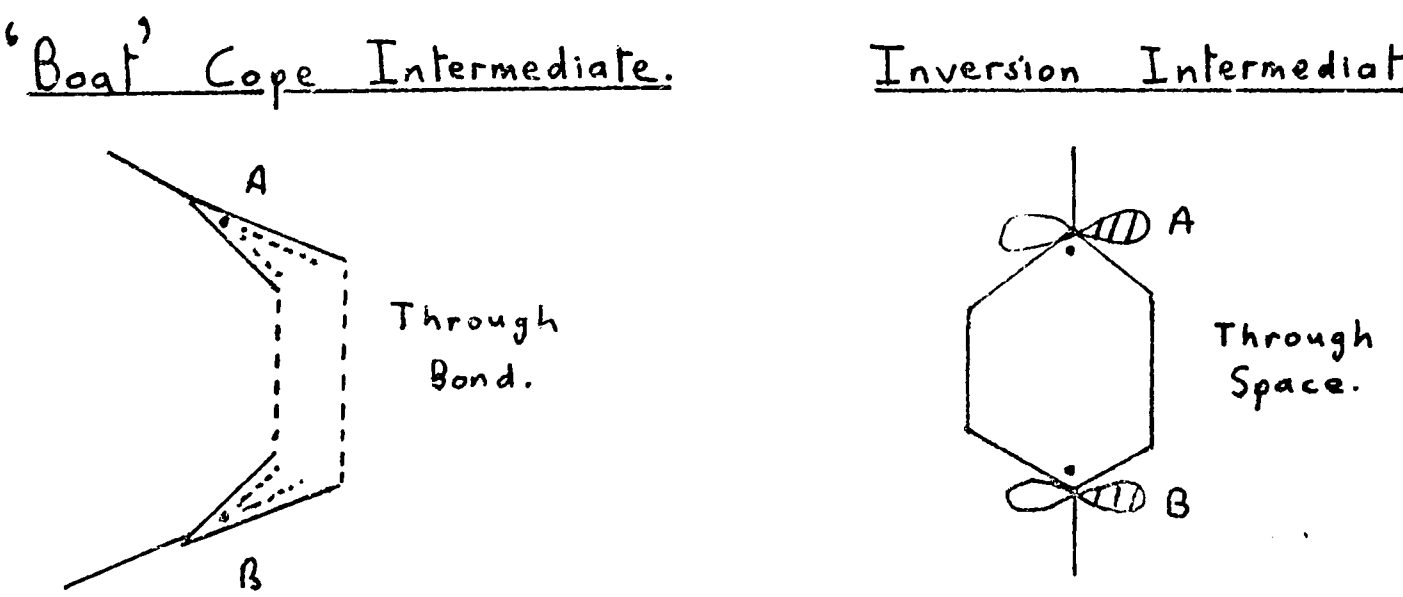


Figure 1.14. Through Bond and Through Space Stabilisation.

General Stereoelectronic Requirements for Organic Reactions and Hückel Molecular Orbital Theory - A Hypothesis.

We are now in a position to present the ideas that initiated this study. The aim, at that time, was to generalise the rules of pericyclic reactions so as to include acyclic transition states. As will be remembered, these rules were based on Hückel molecular orbital theory and aromaticity of transition states. The parameters of the rules were the number of electrons delocalised in the transition state and the parity of the number of negative overlaps in the circuit of the cyclic transition state (i.e. the Hückelness or Möbiusness of the transition state). The approach was again based on Hückel molecular orbital theory and the essential parameter appeared to be the bond orders between non-adjacent atoms in the π-hydrocarbon analogue of the transition state under examination. The reasoning was as follows,

1. The S_N2 has a linear T.S. (transition state) whereas the S_E2 has a non-linear T.S. and proceeds with retention of configuration (Figure 1.9). A partial explanation may be found here in electron correlation, i.e. the Coulombic necessity of keeping the electrons involved in bonding changes as far apart as possible.

2. The E_2 proceeds via the trans conformation and not the cis. This preference may be due to conformational effects since the cis-T.S. will be destabilised by eclipsed conformations and/or electron correlation (if these are distinguishable).

3. Fragmentations These tend to adopt the trans-planar-W conformation. Again this could be due to correlation or conformation effects, but note the resemblance to E_2.

4. S_N2'. Here also syn and anti transition states may occur. The syn-T.S. is preferred, which should be destabilised by conformation effects.

This reaction in particular suggests that other factors are at work.

The question now arising is whether, recognising the possible participation of conformation (steric)/correlation effects, certain particular configurations of atoms in space (i.e. a T.S.) might have an inherently greater stability than others.

The approach is simple-minded and uses as a model for a particular T.S. the π-hydrocarbon analogue (arguments justifying the use of this model are given later). For example, the E_2 reaction, occurring in the trans-planar mode, can be written as in Figure 1.15(a). There are 6 electrons delocalised over 5 atoms. The π-hydrocarbon analogue is thus pentadienylanion. Similarly for the cis-planar E_2 T.S., we take the cisoid conformation of the pentadienyl anion.

It seems that the <u>critical</u> difference between the two conformations is that there is a 1,4 interaction in the cis-T.S. which is absent in the trans-T.S.. This can be represented by a resonance integral, β_{rs}. The change in energy on introducing this resonance integral is given by perturbation theory as

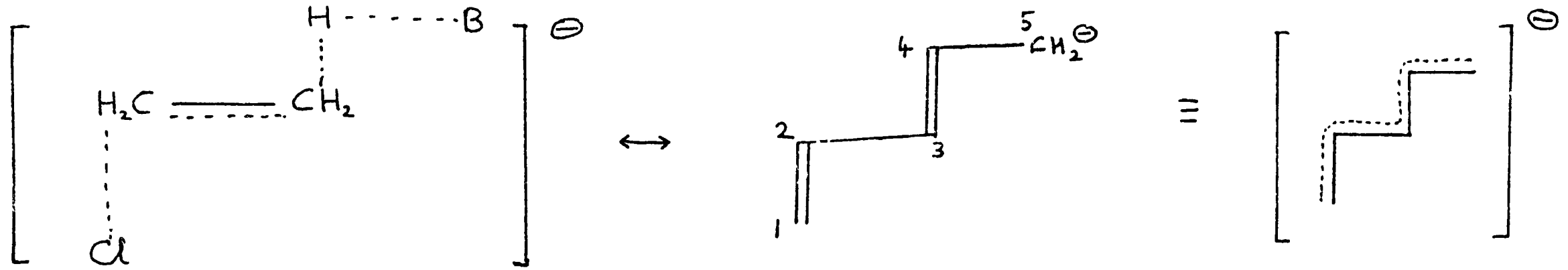
$$\delta E = 2p_{rs} \cdot \beta_{rs}$$

where p_{rs} is the bond order between atoms r and s, and hence is a measure of the stabilising/destabilising effect. For pentadienyl anion, p_{14} = -.212 (From HMO theory). Hence we deduce that cis-E_2 T.S. will be destablised with respect to the trans by an amount related to -.424 β_{14}. It may be that in this way, one can account for the preference for trans-planar E_2 eliminations, and the equivalent "W"-T.S. for fragmentations.

Further examples, are as follows.

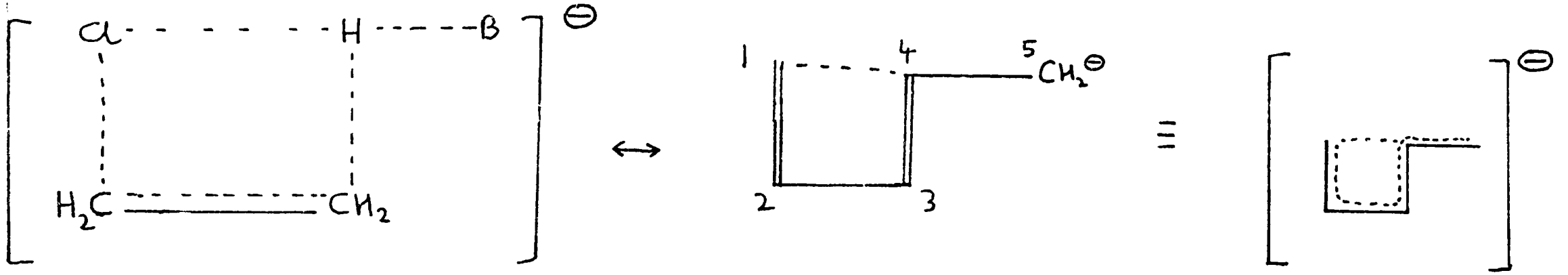
1. (a) <u>S_E2</u>. Two electrons (and three atoms) are involved in the bonding changes, therefore the hydrocarbon analogue is allyl cation. P_{13} for allyl cation is + 0.5, hence the triangular T.S. is more stable,

(a.)



Trans

(b.)



Cis

Figure 1.15. π- Hydrocarbon Analogues of E2 Transition States.

leading to retention.

(b) S_N2. This is now a 4-electron, 3-atom system. Using allyl anion as the model, $p_{13} = -0.5$. A linear T.S. is therefore predicted and reaction proceeds with inversion.

2. (a) S_N2'. This is an example of a 6-electron, 5-atom TS.. It appears that the only difference is the presence of a 1,5 interaction in the syn-TS. P_{15} in pentadienyl anion is +0.33; syn is therefore preferred.

(b) S_E2'. We are now dealing with a 4-electron, 5-atom system - pentadienyl cation, in which P_{15} is - 0.33. The anti TS. is now favoured.

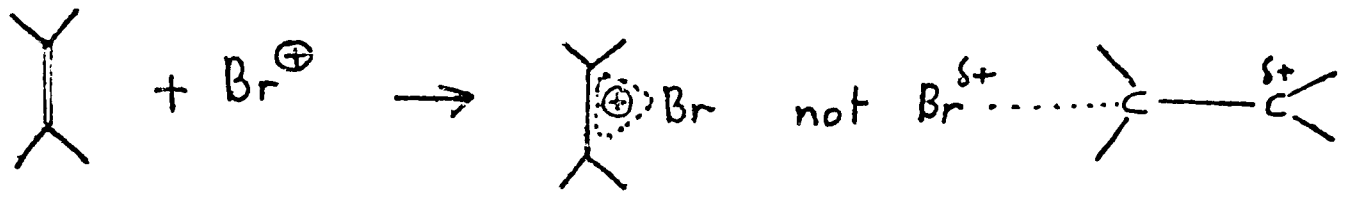
More examples of the applications of this theory are given in Figure 1.16.

Certain aspects of the assumptions on which this simple theory is based still need some justification and it is necessary to be sure of the limits of its applicability.

Firstly, the HMO treatment of a conjugated system assumes (a.) a basis set of C 2p orbitals, all parallel and all perpendicular to the molecular plane and (b.) that $\beta_{rs} = \beta$, if r and s are adjacent, and $\beta_{rs} = o$ if r and s are not adjacent. Our treatment, however, for example in the E_2 TS., is concerned with bonds (σ and developing π) in the molecular plane. It may be said in defence, that the form and energies (in units of β) of the MO's emerging from the HMO treatment are independent of whether we choose σ or π orbitals as the basis set. Thus the pentadienyl anion (a π system) is not an unreasonable model for a σ type TS.

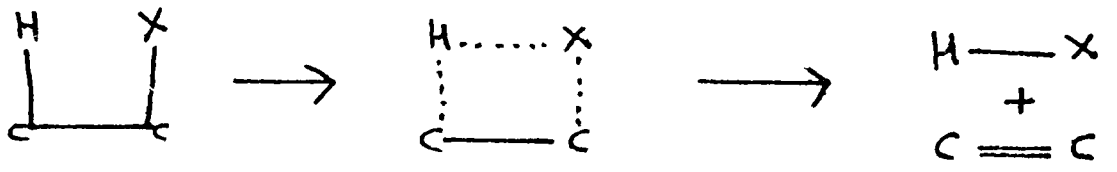
The more significant point is that $\beta_{12} \neq \beta_{23} \neq \beta_{34}$, nor is β_{13} (etc) $\neq o$. The energy of the MO's of the TS. will therefore not be the same as those calculated in the Hückel framework. This however does not invalidate the model as we are not concerned with the energies of the 2T.S.'s

(i). Electrophilic attack on double bonds.

3 ATOM 

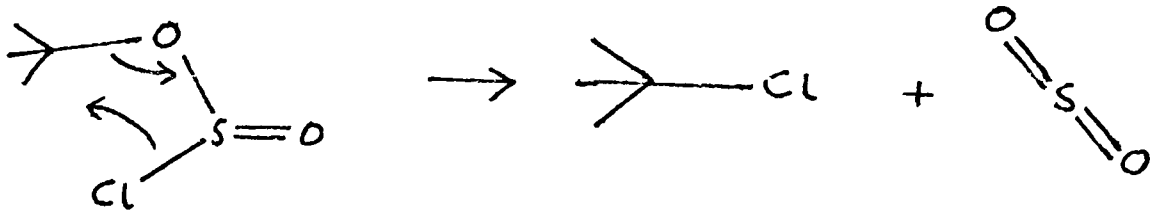
— equivelent to S_E2.

(ii) Cis 1,2 elimination.

4 ATOM 

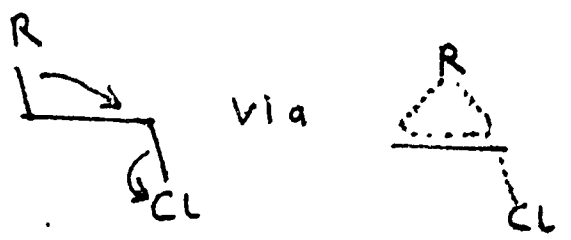
4 atom, 4 electron; $p_{14} = -0.45$. Prediction – strongly forbidden.
Experiment – very rare.

(iii) SNi reaction.



Prediction – strongly forbidden.
Experiment – different non-concerted mechanism operates.

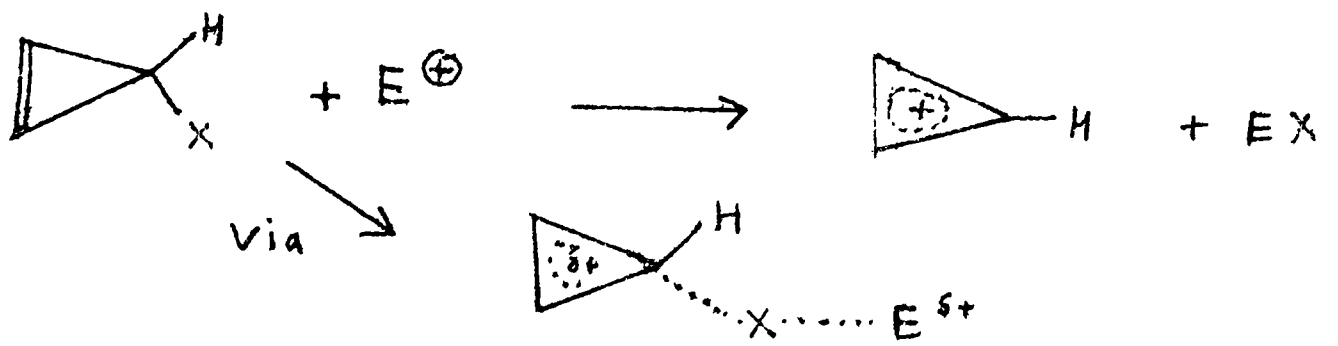
(iv.) 1,2 Shift.

Trans 

4 atom, 4 electron; $p_{13} = 0.0$,
Prediction – allowed.
Experiment – reaction occurs.

Cis 

Prediction – Forbidden.
Experiment – not found.

(v.) 

5 atom, 4 electron; $p_{13} = 0.33$. Prediction – strongly allowed.
Experiment – reaction found.

Figure 1.16. Further Applications of The Simple Hückel Theory

but merely with the difference in energy, to which 2 $p_{rs}.\beta_{rs}$ should still be a reasonable approximation, providing there are not huge differences in the values of β_{rs} for adjacent atoms.

It should also be recognised that this treatment is a perturbational one and hence is only strictly applicable where the perturbing resonance integral is of small magnitude in relation to the β's between adjacent atoms. If the perturbing β does become of significant size, for example where the two atoms become bonded during reaction, the predictions will obviously only hold providing the energy profiles for the 2 T.S.'s do not cross after the initial stages.

It must be mentioned that in certain cases the sign of β_{rs} will also be significant. However the majority of such cases have already been discussed, i.e. pericyclic reactions, where the two transition states differ only in the sign of β_{rs}. If β_{rs} is antibonding, the Hückel bond order factors change sign and might be said to become Möbius bond order factors.

To sum up, it seemed that here was a <u>simple</u> theory which could correlate a large number of known, and possible predict some as yet unknown, stereochemical preferences in organic reactions. It was now necessary to check the assumptions and bases for these predictions at a more sophisticated level of theoretical treatment and analysis.

Chapter 2

THEORETICAL METHODS

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Introduction

The starting point for all calculations reported in this thesis is the Schrödinger equation, the equation of non-relativistic quantum mechanics:

$$H\Psi = E\Psi$$

In principle, any observable property of a system can be calculated by solving this equation with the correct Hamiltonian operator, H, describing the energy of the system. The solutions take the form of a set of wave functions, Ψ, and associated energy levels, E, and may be used to derive all properties of interest. Unfortunately, any system more complex than the hydrogen atom, being a many-body problem, cannot be treated exactly and the most rigorous calculations (called ab initio, because all the integrals involved are explicitly calculated) make several assumptions to ease solution of the above equation. These approximations are well-founded, and ab initio calculations, which make up a significant proportion of the work in thesis, are theoretically sound. Nevertheless they ignore relativistic and correlation effects (discussed below) and become computationally very time-consuming as the molecular size increases. There is also some difficulty in achieving sufficient accuracy for chemical problems. The heat of formation of methane for example, is less than 0.1% of the ab initio molecular energy, and to calculate such properties requires a degree of precision only possible for very small molecules. Thus a hierarchy of approximate, semiempirical methods has developed. Semiempirical calculations are more sensitive to changes in the outer electrons than are ab initio ones, and are of course much faster. They suffer the disadvantage of being on less certain theoretical foundations, and consequently must be used

more carefully. The MINDO programs of Dewar (1969,1969a,1970,1970a, 1975b) have probably been the most thoroughly tested, and applied, semiempirical methods and have been used for a large part of the work in thesis.

The Molecular Orbital Method

The first simplification of the Schrödinger equation was due to Born and Oppenheimer (1926). This approximation allows the nuclei of a molecule to be treated as a stationary framework and the Hamiltonian to be written in terms of electronic energies alone. The electronic wave function is thus obtained for a particular configuration of nuclei, and addition of the nuclear repulsion energy gives the total energy for that configuration. Thus a potential energy surface may be obtained as a function of the nuclear coordinates.

With this approximation, the electronic Schrödinger equation may be written,

$$(-T_e - V_{en} + V_{ee})\Psi = E\Psi$$

where the operators are, Te for the electronic kinetic energy, V_{en} for the nuclear-electron attraction, and V_{ee} for the interelectron repulsion. In order to evaluate the interelectron repulsion we require a knowledge of the interelectronic distance, r_{ij}, - in other words a solution of the wave equation isneeded in order to write it down! The Self-Consistent Field approximation overcomes this problem, by assuming that each electron moves in an average potential due to all the other electrons

$$\sum_i \sum_{j<} \left(\frac{e^2}{r_{ij}} \right) \rightarrow \sum_i \left(\frac{e^2}{r_{ij}} \right) \text{ average over j}$$

* The one-electron wave functions are further divided into a product of spin and spatial parts. This may be considered as a further approximation.

Thus a trial wave function is guessed at the start of a calculation and used to construct the average potentials. The equation is solved and the solutions are used to form new, hopefully better, potentials so that calculations proceed iteratively until successive potentials are unaltered - a self-consistent field.

The last important approximation to be introduced is the Orbital approximation, which allows each electron to be represented by an independent mathematical function called a molecular orbital. The total wave function of the molecule is then a product of these one-electron wavefunctions. In fact this simple product is insufficient as it does not conform with the Pauli principle. A linear combination of products is used, which satisfies this principle and is termed a Slater determinant. It can be shown that the exact solution of the electronic equation may be expressed as a linear, but unfortunately infinite, combination of Slater determinants, (See e.g. McWeeny and Sutcliffe (1969)). It is usual to use only one or two determinants, which is the case in the work to be reported. This greatly simplifies the physical interpretation of the results. *

The Hartree-Fock and Roothaan Equations

With the above assumptions, the Schrödinger equation for a closed-shell molecule (i.e. one in which the filled orbitals occur in pairs with the same space function but different spin functions) takes the form of the Hartree-Fock (1928,1930) equations, where there is one such equation for each electron, i, represented by a molecular orbital, ϕ_i.

$$\left\{ H^{core} + \sum_j (2J-K)_j \right\} \phi_i = \varepsilon_i^{s.c.f.} \phi_i$$

The Hamiltonian consists of a one-electron part (the nuclear-electron attraction, H^{core}) and a two-electron part (the electron-electron repulsion). The two-

electron Hamiltonian contains the operators J and K, the Coulomb and exchange operators respectively, the corresponding integrals of which are

$$\text{Coulomb:} \quad J_{rs} = \int \phi_r^*(1)\, \phi_r(1) \frac{1}{r_{12}} \phi_s^*(2)\, \phi_s(2)\, d\tau_1\, d\tau_2$$

$$\text{Exchange:} \quad K_{rs} = \int \phi_r^*(1)\, \phi_s(1) \frac{1}{r_{12}} \phi r(2)\, \phi_s^*(2)\, d\tau_1\, d\tau_2$$

The Coulomb term is a simple electrostatic repulsion between charge clouds, while the exchange integral is less repulsive because electrons of parallel spin correlate their motions to reduce repulsion. This is a purely quantum mechanical effect and arises from the Pauli principle. When, as is usually the case, the molecular orbitals are constructed from a linear combination of atomic orbitals of the molecule (theLCAO method), the resulting equations, which form the basis of all the molecular orbital calculations of relevance to this thesis, are called the Roothaan (1951) equations

$$\sum_s (F_{rs} - \varepsilon_i S_{rs}) C_{si} = 0$$

$$F_{rs} = H_{rs} + \sum_{uv} P_{uv} \left[(rs|uv) - \tfrac{1}{2} (ru|sv) \right]$$

where F is the Fock matrix (derived from the previous set of molecular orbitals), C is the matrix of coefficients of the atomic orbitals in the molecular orbital, ϕ_i, and S is the overlap matrix, defined by

$$S_{ij} = \int \Psi_i^* \cdot \Psi_j \, d\tau$$

In a few of the calculations to be reported, open-shell configurations of molecules are involved, in which there are incompletely filled pairs of molecular orbitals. Thus the Slater determinant is constructed from orbitals paired to form a closed-shell part, plus unpaired orbitals forming an 'open-shell' part. Due to the restrictions on the

closed-shell part of the wave function, it is relatively easy to evaluate the energy using Slater's rules (1929,1931), which express the electronic energy as a sum of one-electron and two-electron integrals. It may be noted that if the orbitals are chosen simply to minimise the energy, they will not be paired into a closed-shell part, and the resulting 'unrestricted' wave function is not an exact eigenfunction of the spin operators, though it may be very close. This type of calculation has not been used in this work.

The type of mathematical function used to represent an atomic orbital depends on two criteria. Firstly how well it actually represents the orbital, so that the number of functions used may be small, and also how easy it is to evaluate the molecular integrals based on these functions. These are two common types, the Slater type function (1930) and the gaussian function due to Boys (1950). These are respectively of the general form,

$$Y_{Lm}(\theta,\phi)\, r^{n-1}\, e^{-\zeta r}$$

$$Y_{Lm}(\theta,\phi)\, r^{n-1}\, e^{-\zeta r^2}$$

where Y_{Lm} describes the angular dependence of the function and the rest describes the radial dependence. The Slater functions are a better representation of the wave function but evaluation of integrals over four centres is difficult. For this reason gaussian functions are preferred for polyatomic systems, although many more are required to achieve comparable energies. Usually a linear combination of gaussian functions is preselected to represent an atomic orbital. Sometimes these so-called contractions are chosen to resemble Slater functions. It is found that three gaussians per Slater are adequate to represent valence

orbitals, but at least six are required if core orbitals are of interest. In the ab initio work to be reported, gaussian basis functions were employed.

Ab initio calculations

Ab initio calculations are those in which only the previously described approximations are made and all molecular integrals are calculated exactly. However the results of ab initio calculations themselves differ appreciably from exact wave functions, due to three defects.

1. Finite basis set. If an infinite set of basis functions is used it is possible to obtain the Hartree-Fock orbitals exactly, the corresponding energy being the Hartree-Fock limit. In practice of course, only a limited basis set is used, so that the energy obtained is above the Hartree - Fock limit. In fact, it is possible to get near this limit with a relatively small basis set, but small improvements in energy then require increasingly large computational efforts.

2. The relativistic energy. The inner electrons, especially in heavy atoms, have a large enough kinetic energy to approach appreciably close to the speed of light and thus have a relativistic energy. This energy cannot be calculated, but it may reasonably be expected to remain unaffected by chemical changes, and so can be ignored when differences in properties are calculated.

3. The correlation energy. The average potentials used in the S.C.F. method do not accurately represent the instantaneous correlation of electronic motions which minimises interelectronic repulsions. This is only partly allowed for by the inclusion of exchange integrals, which in any case apply only to electrons with parallel spins. The correlation

* There have been several other approaches to the problems of correlation energies. The 'pair population' model of Hollister and Sinanoğlu (1966) is used by Snyder and Basch (1969) to estimate the changes in intraatomic correlation energies. The parameters required are the atomic orbital populations and the pair correlation energies. The remaining differences between the calculations and experimental values of heats of reactions allows one to deduce empirical corrections for the interatomic correlation energies.

The Generalised Valence Bond theory developed by Goddard (1973) concentrates on the atomic orbitals of sets of atoms rather than on molecular orbitals. This allows one to represent the processes of excitation and bond formation/dissociation more accurately since the double-occupancy restriction of H.F. wave functions is lifted. It may be noted that this occurs by introducing singly occupied orthogonal singlet-coupled orbitals, which makes the S.C.F. cycling much more complicated and time-consuming. Examples of Goddards studies (1974, 1974 a) are his work on ozone and methylene/ethylene.

energy cannot be calculated and is quite a problem in ab initio work. It has been shown (Allen et. al. (1963)) to depend on the pairing of electrons and so, when pairings of electrons do not change, the difference in correlation energy between different systems is small.

One procedure for estimating correlation energy is the method of configuration interaction. The virtual (i.e. unfilled) orbitals of a single-determinant calculation may be used to construct other configurations, and an appropriate linear combination found by diagonalising the matrix of the Hamiltonian. However this procedure is prohibitively lengthy for realistic bases. It is therefore necessary to limit the number of configurations, but there is no general rule as to the type of configuration most likely to make a significant difference to the energy. *

It is not easy to relate the results of ab initio calculations, involving completely delocalised orbitals, to the usual picture of a molecule in terms of two - centre bonds. However it is possible by a unitary transformation, which does not affect the total wave function, to localise the molecular orbitals in particular regions, using some criterion such as that of Foster and Boys (1960). This cannot be done completely and part of each orbital ('tails') remains on other centres than the two principle ones.

An often used method of decomposing wave functions, due to Mulliken (1955), is termed 'overlap population analysis'. The eigenvectors are squared and multiplied by the orbital occupancy (n_i = 0,1 or 2) and the total electron density obtained as a function of the coefficients and the overlap matrix elements

$$\Sigma\, pr = \Sigma_i \left[\Sigma_r\, ni.c^i_{rr} + 2\,\Sigma_{r\neq s}\, nic^i_{rs}.Srs\right]$$

where i denotes the molecular orbital. The components of the first summation are assigned to the atom on which the basis function Xr is

centred and the components of the second summation are simply divided equally between the two centres of X_r and X_s. For each basis function a charge is assigned as follows

$$Pr = \Sigma ni.c^{i}_{rr} + \sum_{r \neq s} ni.c^{i}_{rs} S_{rs}$$

and the gross charge on a given centre is then obtained by summing the contributions from each basis function on that centre.

Two ab initio series of programs were used for the work in thesis. ATMOL/2 was devised by Hillier and Saunders (1970) and GAUSSIAN 70 by Pople and co-workers (1969-72). Further details of these specific programs are given in Appendix 1.

Semiempirical methods

In view of the lengthiness of ab initio procedures, several methods have been proposed for producing wave functions semiempirically. Since ab initio calculations themselves have the above limitations, it might be thought that more approximate methods have little chance of achieving chemically useful results. There are, however, compensating features in semiempirical calculations, which account for their rather remarkable success.

The justification of semiempirical methods is that many of the largest integrals in ab initio calculations, especially those involving the inner electrons, are virtually unaffected by the chemical environment and may be equated to empirical parameters, characteristic of the atom concerned. Thus all semiempirical procedures make the valence approximation. In this the 1s electrons on atoms other than hydrogen are taken into the atomic core. Interestingly, it has been shown using X-ray photoelectron spectroscopy (Siegbahn et al., 1969) that binding energies do vary significantly with chemical change, but this probably reflects more pronounced changes in the outer electrons. It

is also common to expand the wave function in terms of Slater type atomic functions, as the integrals derived from these which cause great difficulty in ab initio programs are parameterised.

The empirical parameterisation can be approached in two ways, which are related to the distinctions made previously between the ab initio and semiempirical 'schools'. Pople, representing the former, uses empirical parameters which often have a clear physical meaning (e.g. ionisation potential) and attempts to reproduce rigorous ab initio results. This has the advantage of being on a theoretically sound basis for checking of the results and is the basis of CNDO and INDO parameterisation (see below).

Dewar on the other hand, representing the chemical 'school', has pointed out (1970) that the most reliable S.C.F. calculations can be in error by ± 100% for the heats of atomisation of diatomic molecules. Also these errors are not even constant for molecules formed from the same set of atoms (see e.g. Snyder, 1967). Therefore there seems to be little purpose in trying to reproduce these errors, as one would presumably then have to introduce empirical corrections to fit the results in with experiment. An alternative procedure is to try to improve the practical results of quantum mechanical calculations, by treating some of the integrals appearing in them as parameters. A criticism which has been levelled against this approach is that different parameters are needed for different sets of compounds or different molecular properties. This is in fact the case for many semiempirical methods, but not so with Dewar's MINDO programs, and as he has recently pointed out (1975a), this can probably be attributed to the fact that insufficient care has been taken in carrying out the previous parameterisation procedures. His versions of MINDO have been shown to be of extensive

use in many branches of chemical investigation and in particular fill the four main requirements of a predictive theory.

(1) The results must be chemically accurate.

(2) The results must be reliable, in comparison with experiment.

(3) No assumptions must be made concerning geometries etc..

(4) The cost of calculations for systems of chemical interest must not be excessive.

The major approximation common to all semiempirical methods will first be described and then the details of MINDO/2 will be given.

The Neglect of Differential Overlap (NDO)

The major bottleneck in ab initio calculations is the evaluation of the electron repulsion integrals. It happens that the ones which are hardest to calculate, those involving the overlap distribution, $\phi_A(1)\phi_B(1)$ with $A \neq B$, are also the smallest. An approximation introduced by Pariser and Parr (1953) and Pople (1953) takes advantage of this, and its most stringent form is called zero differential overlap,

$$(rs|uv) = (rr|ss).\ \delta_{rs}.\delta_{uv}$$

$$S_{rs} = \langle r|s\rangle = \delta_{rs}.Xr.Xr$$

where $\delta_{rs} = 0$ if $r \neq s$, $=1$ if $r = s$

Most semiempirical methods invoke this approximation to some degree, while taking care that the solutions are unaltered by rotation of the axes (while true for the full Roothaan equations, this does not automatically apply to approximations to them).

MINDO/2

MINDO is a Modified version of the INDO method of Pople et. al. (1967), and was devised by Dewar and co-workers. It is designed to

calculate heats of formation as accurately as possible. There have been several versions of this program, as it has been progressively improved and updated. The latest version, MINDO/3, has only now become freely available for workers outside Dewar's group. The version used in the work to be reported is MINDO/2, as modified by McIver (1971) and Komornicki, in order to achieve efficient location of equilibrium geometries. INDO is an acronym for intermediate neglect of differential overlap and implies that the NDO approximation has been relaxed slightly, in that electron repulsion integrals of the type $(rs|rs)$, are included if r and s are on the same atom. This also allows one to differentiate between singlet and triplet configurations.

The parameterisation procedure and rationale is as follows:

(i) The one-centre electron repulsion integrals are derived from the atomic spectra of first row atoms.

$$\left.\begin{aligned} (ss|pp) &= (ss|ss) = F^0 \\ (sp|sp) &= \frac{G^1}{3} \\ (pp|pp) &= F^0 + \frac{4}{25} F^2 \\ (pp|p^1 p^1) &= F^0 - \frac{2}{25} F^2 \\ (pp^1|pp^1) &= \frac{3}{25} F^2 \end{aligned}\right\} \quad \text{Slater - Condon parameters.}$$

(ii) The one-centre core electron integrals, U_{ss} and U_{pp}, are also derived from atomic spectra data.

(iii) The repulsion between atomic orbitals on centres A and B are given the common value, γ_{AB}, as are the two-centre core-electron integrals,

$\langle r_A | V_B | r_A \rangle$.

The expression for γ_{AB} is derived from that given by Ohno (1964) and Klopman (1965),

$$\gamma_{AB} = e^2 \left[R^2_{AB} + 0.25 \, (P_A + P_B)^2 \right]^{-\frac{1}{2}}$$

$$\text{where } P_i = e^2 / F^o_i$$

$$\text{Hence } \gamma_{AB} \rightarrow \tfrac{1}{2} \left[F^o_A + F^o_B \right] \quad \text{as } R_{AB} \rightarrow 0$$

$$\rightarrow e^2 / R_{AB} \quad \text{as } R_{AB} \rightarrow \infty$$

F^o being the average one-centre Coulomb repulsion integral.

(iv). The off-diagonal core matrix elements, β^c_{rs}, also known as the resonance integrals, are represented by functions that conform to the physical requirements and contain a parameter that is fitted, by regression analysis, to experiment, there being one for each pair of atoms A and B,

$$\beta^c_{r_s} = B_{AB} . S_{rs} . (I_r + I_s)$$

Where B_{AB} is the parameter, S the overlap integral, and I_r and I_s the valence-state ionisation potentials of the orbitals on atoms A and B.

(v) The core repulsion function also contains a parameter determined by regression analysis from experiment, to aid the sensitive balancing of electronic and nuclear effects needed in calculating heats of formation.

$$CR_{AB} = ER_{AB} + (Z_A \, Z_B \, e^2 / r_{AB} - ER_{AB}) . e^{-\alpha_{AB} r_{AB}}$$

$$e^{-\alpha_{AB} r_{AB}} \rightarrow 0 \quad \text{as } r_{AB} \rightarrow \infty$$

$$\rightarrow 1 \quad \text{as } r_{AB} \rightarrow 0$$

* It may be noted that several minor shortcomings of MINDO/2 have been observed during its applications by other workers. Besides those mentioned elsewhere, two others are of relevance. Firstly, bond angles at atoms with lone pairs are poorly represented. Thus water is predicted to be linear. This affects some of the equilibrium geometries calculated elsewhere, but does not affect the conclusions. Similarly, the ordering of molecular orbitals, especially unfilled ones, are not always correctly predicted, if the results of ab initio calculations are taken as a guideline. However, within the σ and π sets, the ordering is generally correct and it is only the mixing of these sets which may be at fault. Thus our later conclusions will be seen to still hold both in their understanding and predictions of reaction preferences.

Thus the core repulsion, CR_{AB} is equal to the electron-electron repulsion between neutral atoms, ER_{AB}, when r_{AB} is large, in order that there should be no long range Coulomb interactions between neutral atoms. Physical intuition also suggests that as $r_{AB} \to 0$, CR_{AB} should tend to the point charge potential $Z_A Z_B e^2/r_{AB}$, where Z_A and Z_B are the formal charges on the cores of the two atoms, which is the case with the above function.

The matrix elements of the core and Fock matrices are therefore given by the following expressions:

Core matrix :
$$H_{rr}^{AA} = U_{rr} - \sum_{B \neq A} C_B \gamma_{AB}$$
$$H_{rs}^{AA} = 0$$
$$H_{rs}^{AB} = \beta_{rs}^{c}$$

Fock matrix :
$$F_{rr}^{AA} = U_{rr} + \tfrac{1}{2} qr\,(rr|rr) \quad \text{(core)}$$
$$+ \sum_{s \neq r}^{(A)} q_s\left[(rr|ss) - \tfrac{1}{2}(rs|rs)\right] \text{(other electrons on A)}$$
$$+ \sum_{B \neq A} (Q_B - C_B)\gamma_{AB} \quad \text{(other electrons)}$$
$$F_{rs}^{AA} = P_{rs}\left[\tfrac{3}{2}(rs|rs) - \tfrac{1}{2}(rr|ss)\right]$$
$$F_{rs}^{AB} = \beta_{rs}^{c} - \tfrac{1}{2} Prs.\gamma_{AB}$$

Where C_B is charge on core B, q = electron density of atomic orbital, Q = total valence-shell electron density, P = bond order matrix.

The above matrix elements were used in order to partition the energy expression, for reasons that will be explained later. Details of this breakdown, and other technical details of the particular MINDO/2 program used (OPTMO). including the features added for the work in thesis, are given in Appendix 1.

OPTMO

The MINDO/2 program has been used by McIver (1972) to form the basis of a program which can be used to locate reactants, products and transition states on a potential energy surface. Previously this was achieved either by assuming a geometry and reaction pathway, which is fast but theoretically unsound, or by allowing a limited amount of geometrical relaxation of the nuclear configuration as reaction proceeds. The latter is a long and tedious process since a set of N atoms has 3N-6 degrees of freedom, each of which must be varied indepently, often several times. As three points are required for each parameter variation, a system of nine atoms would require > 100 calculations.

A far more efficient plan would be to allow all parameters to be varied simultaneously by amounts related to the forces which are acting on the atoms. This is the physical basis of McIver's method. In order to do this, it is obviously necessary to calculate the internuclear forces that are present in an array of atoms. In other words, one must evaluate the matrix elements of the gradient of the potential energy function with respect to the 3N Cartesian coordinates, qi, of the N atoms of the system. McIver and Komornicki, using the Murtagh-Sargent (1970) method, find these derivatives analytically by direct differentiation of the MINDO expression for the total energy. This is only feasible, in terms of the extra computer time required, for semiempirical methods, again because three and four centre terms are ignored in these calculations. This, of course still further increases the disparity in cost between semiempirical calculations and ab initio calculations, as will be shown below.

In order to locate an equilibrium ground state geometry, we must search for a point at which all elements of the gradient energy matrix are zero. Thus a calculation is performed with an assumed geometry and

the elements of this matrix are evaluated. The atoms are now moved by amounts proportional to the matrix elements and a calculation again performed. This is repeated until all elements of the gradient energy matrix are below a certain tolerance. As an example, the norbornyl cation, $C_7H_{11}^{\oplus}$ (48 coordinates), requires 25 gradient S.C.F. calculations to determine the equilibrium geometry, whereas at least 500 ab initio calculations, varying parameters one by one, would be required. The overall cost difference between the two processes has been judged to be 5 orders of magnitude greater in the ab initio case!

To identify a transition state, at which point all elements of the gradient energy matrix also equal zero, is however a little harder and two methods have been used in the calculations to be reported. If it is likely that the transition state is of higher symmetry than either the reactants or the products then a quick method is to input a species approximating to the transition state with the required higher symmetry. It can be shown that the energy minimisation method preserves the symmetry of the input species and hence the atoms cannot resort to products or reactants. When one has located what one believes to be the transition state, remembering the warnings on assumed symmetry of a T.S. it is worthwhile ensuring that 'geometry optimised' distortion to a less symmetrical species (with restraints to prevent reversion to reactants or products, if necessary) does not produce a more stable species.

A more general method to locate a T.S. is to choose one or more reaction coordinates; e.g. bond lengths of bonds being formed/broken, or bond angles, and vary all other parameters at fixed values of these coordinates. This potential surface scan is brought about by putting the elements of the gradient energy matrix related to the fixed parameter equal to zero. Again one must ensure that one has found the transition state

and not merely a local stationary point. This can usually be done by inspection but otherwise 'distorting' calculations or more sophisticated evaluations must be used. This was not found to be necessary in the cases considered, which will now be described.

Chapter 3

STEREOSPECIFICITY IN ORGANIC REACTIONS

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Introduction

Before reporting and discussing the results, it is necessary to mention certain practical details.

i. The OPTMO program was not originally available and when received had to be translated so that it could run on the Oxford University ICL 1906A computer. This was some time after the work in thesis had begun and therefore all previous semiempirical calculations had employed a simple version of MINDO/2 with no optimisation procedures. When used, this will be referred to as the OLDMINDO program.

ii. Similarly GAUSSIAN 70, with its very fast integral evaluation and geometry optimisation packages, was received after a number of ATMOL ab initio calculations had been carried out. Also the GAUSSIAN 70 package was put on the IBM 370/195 machine at Harwell, on which limited time was available. Although this is a much faster machine than the ICL 1906A, the time allocated precluded extensive optimisation of all but the simplest of molecules.

iii. All other smaller programs were used on the ICL 1906A computer because of vastly superior communications and storage facilities possible with this machine. These included programs which

(i) converted bond angles and bond lengths to Cartesian coordinates (CARCOR).

(ii) Plotted Cartesian coordinates of molecules (OXPLOT).

(iii) Performed various manipulations of matrices, OPTMO output etc. (MATRIX, EDSEE, DIAG etc.).

The results follow in roughly chronological order. This is not always the case obviously, as some later calculations made it necessary

to expand and complete previous calculations. Also a major part of the work involves analysis and breakdown of the results obtained. This will mainly be reported in each section, and general conclusions concerning all the analyses will be left until the end.

1. Ab Initio Calculations on Allyl and Butadiene Species.

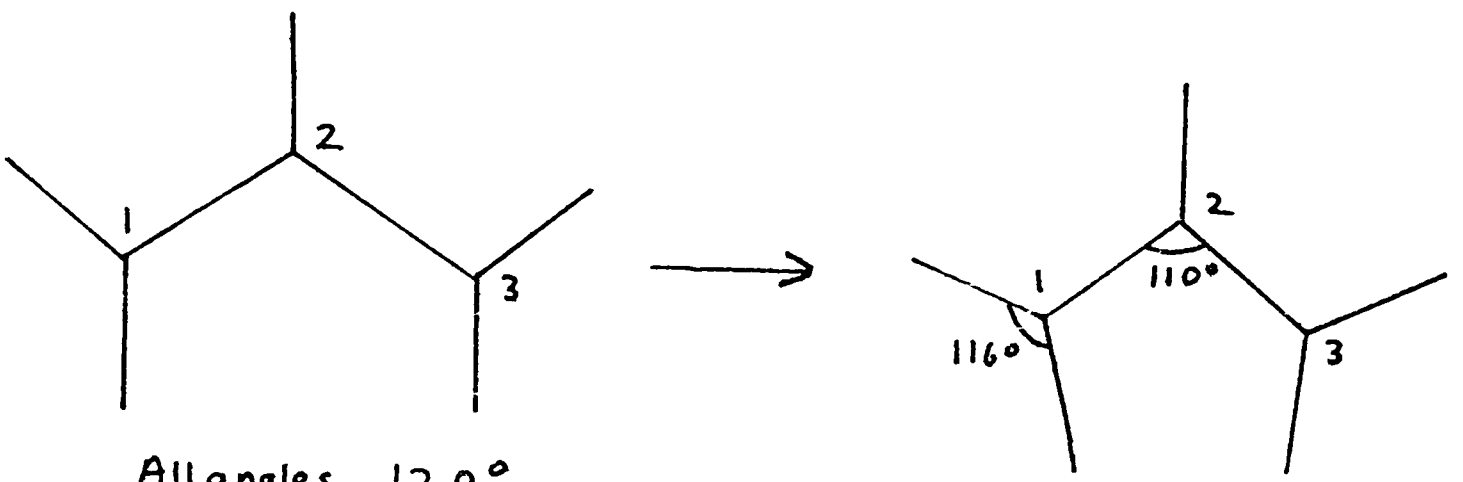
It was first necessary to determine whether the Hückel 'bond order factors' were of any relevance in the context of more sophisticated calculations, and if they were found to be so, to examine why. To do this, ATMOL calculations were performed on allyl and butadiene species, containing a varying number of electrons. The geometries were perturbed slightly and the calculations were repeated.

(a) Allyl

The change shown in Figure 3.1 was investigated for the allyl cation, radical and anion and the energy increases were determined. The optimum geometry of the unperturbed allyl system is that derived by Farnell (1974), who also used the ATMOL program. The energy changes are seen to follow the same order as the Hückel bond order factors predict. Similarly, the π-bond orders derived from the ATMOL calculations and the electron density changes at the terminal carbons follow this order. It might appear therefore that the π orbital changes are the dominant terms.

(b) Butadiene

This is possibly a more interesting test, as the bond order factors do not change linearly when electrons are added to the π system. The perturbations shown in Figure 3.2 were studied for butadiene and the radical cation and anion derived from it. Again the relative energy changes were obtained together with indices of possible relevance. The geometry used for trans-butadiene is that experimentally determined by Bastiansen (1950).



All angles 120°

C – H's 2.04 a.u.

C – C's 2.711 a.u.

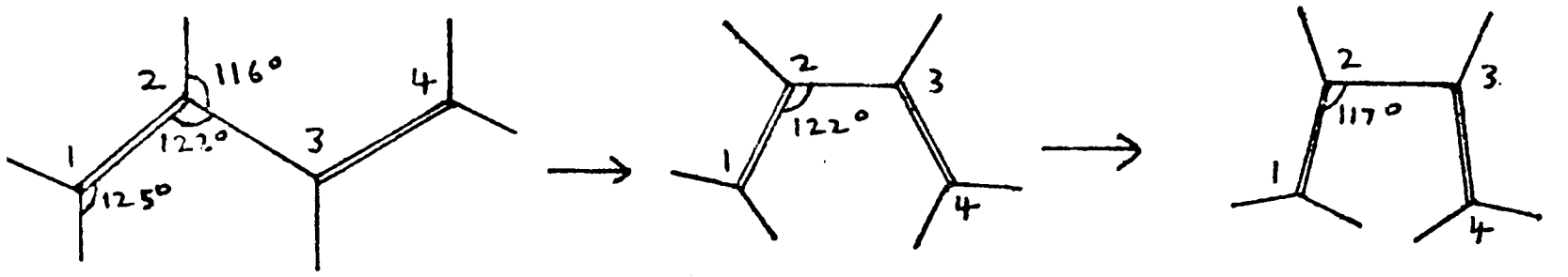
	CATION	RADICAL	ANION
Energy Increase (Kcal/mole)	1.07	4.78	10.99
Hückel Bond order factor	0.5	0	−0.5
ATMOL π Bond order factor ($\sum^{\pi} c_1 c_2$)	.325	−.154	−.635
Total electron density change, $\Delta \mathbf{C}_3$	0.0	−0.009	−0.015
π electron density change, $\Delta \mathbf{C}_3^{\pi}$	0.010	0.004	−0.002

(negative sign means less electron density in perturbed species)

$\mathbf{C}$ = carbon electron density

c = coefficient of an atomic orbital in a molecular orbital.

Figure 3.1 Perturbation of Allyl Systems



tr c bc

C–H's 1·06Å
C=C 1·35Å
C–C 1·46Å

(All bond lengths as in tr)

(i) tr → c

	RADICAL CATION	NEUTRAL	RADICAL ANION
Energy Increase (Kcal/mole)	2·17	3·56	2·01
Hückel Factor	−0·085	−0·447	−0·085
ATMOL π-Factor	−0·001	−0·306	0·043
ΔC_4 (Total)	0·001	−0·010	−0·011
ΔC_4^{π}	0·017	−0·019	−0·023

(ii) c → bc

Energy Increase (Kcal/mole)	5·30	7·68	8·94

(iii) Overall energy changes (tr → bc) 7·47 11·24 10·95

Figure 3.2 Perturbation of Butadiene Systems

One observes that with respect to the change from trans- to cis-butadiene, the energy increases are in agreement with the Hückel bond order factors. However, on increasing the 1,4 interaction (c→bc), 'steric' factors (i.e. σ-electron effects) appear to predominate, although the change in the neutral molecule is still greater than might be expected, if it were intermediate between the cation and the anion.

When one studies the details of the trans to cis change, it is found that the simple explanation used for the allyl case does not apply. Although the ATMOL π-bond order factors do vary roughly in the same way as the Hückel factors, the electron density changes do not. It would appear that the reason the allyl example was deceptively simple, is that σ and π effects in those species varied in unision. Whereas in the butadiene system, although a perturbation of the neutral species is seen to involve a shift of electron density away from C_4 greater than that expected if it were an intermediate case, in all breakdowns, the terminal electron density changes become more negative as electrons are added. It is therefore necessary to find some other index or combination of indices which might prove to be more useful in correlating the successful HMO predictions with the more complex calculations.

2. Bonding Indices for Semiempirical and Ab Initio Calculations

Although the use of electron density changes and bond order factors might have been inappropriate in the above systems, because of the small perturbations involved, it is important to note certain drawbacks associated with them.

a. It is not necessarily the case that $\Delta\mathbf{C}_A$ or $\Sigma c_A c_B$ alone would give an index of bonding, as in some systems, 1-centre energy terms may be dominant (related to $\Delta\mathbf{C}_A$) and in other systems multicentre terms will predominate

(a function of $\Sigma C_A C_B$ etc.). This itself is a simplification as some multicentre terms also depend on C_A, e.g. $\langle \chi_r^{(A)} | -\frac{Z_B}{r_{rB}} | \chi_r^{(A)} \rangle$ is a 2-centre energy term, but only a 1-centre atomic orbital term. Of course the nuclear-nuclear terms are not related to either C_A or $\Sigma C_A C_B$!

b. Even if one set of terms, i.e. 1-centre or multicentre, were dominant, as could well be the case in the above examples, it is by no means certain that the change in the 'bond energy' term, ΔE_{AB}, is proportional to $\sum_r^A \sum_s^B C_r C_s$ (r and s are the atomic orbitals on centres A and B). Only for large energy differences will this always hold, and certainly this will not be so for the small energy changes associated with conformational peferences.

N.B. The above is <u>not</u> a criticism of the use of bond order factors as valid bonding indices in the simple Hückel approach, since it is consistent <u>within that context</u>, with the assumptions inherent in the approximation. However in semiempirical methods etc., the assumptions and energy evaluation are different and any bonding indices must be examined in the light of these new assumptions. Of course, the assumptions themselves must also be critically studied in order to ascertain whether the method itself is appropriate to the problem being considered.

It is of interest to mention some of the indices that have been used in connection with various semiempirical methods of the MINDO type.

i. <u>Wiberg's (1968) bond index</u>.

This is defined as follows,

$$\text{Index} = (P_{AB})^2, \text{ where } P_{AB} = \sum_r^A \sum_s^B C_r C_s$$

This is obviously nonsense for non-bonded atoms (which will be of interest) as it is always positive and thus highly bonding and highly antibonding situations would be equivalent. It might be thought to be appropriate to bonded atoms, but if one actually investigates the filled orbitals of an organic molecule, it is found that many contain nodes between main atoms, which would still give a positive contribution to the index.

ii. Epiotis' (1973) bond order.

This is the P_{AB} of Wiberg's index, $= \sum_{r}^{A} \sum_{s}^{B} C_r C_s$. The problem associated with Wiberg's index has been removed but we have two equally important ones in its place. Firstly it is rotationally variant and a change in the direction of the coordinate axes will change its value. (This has been confirmed by simple calculations, which show that this change is of significance and cannot be ignored). However Epiotis uses a consistent coordinate system when looking at changes among a series of related compounds. But a second, more important, difficulty arises. Epiotis 'shows' by means of this index, the effects of π bond-lone pair interactions in haloethylenes. However because no distance function is introduced, (e.g. S_{rs} or $\frac{1}{r_{AB}}$), it is not true to say that these interactions have been shown to be the decisive ones. In fact, Kollman (1974) has recently proved that Epiotis was mistaken in assigning the cause of stability to the above effects, for precisely this reason.

iii. Overlap population analysis.

This has been mentioned previously, and the overlap population is given by,

$$\sum_{r}^{A} \sum_{s}^{B} C_r C_s S_{rs}$$

In ab initio calculations, this represents part of the electrons, whereas in semiempirical calculations the molecular orbitals are normalised

such that

$$\sum_{r}^{(i)} C_r^2 = 1$$

It is for this reason that Epiotis indirectly suggests that use of this index is inconsistent with a ZDO method. Its advantages, however, strongly outweigh this criticism. Besides being rotationally invariant, and differentiating between s and p electrons, the inclusion of an overlap function prevents the mistaken conclusions arrived at by Epiotis. Also, although the electron is not represented by such terms, these terms are involved in the energy evaluation (i.e. the Hamiltonian matrix elements), which is the observable of importance. For these reasons, this index was used for initial stages of analysis and will be mentioned where it highlighted certain unusual features of the results.

One further problem remains with this index. Some terms which make up the Hamilonian matrix elements depend on S_{rs} and some on γ_{AB}, independent of the atomic orbitals involved - note this refers only to the semiempirical methods. Thus we require a function of the form,

$$\left[\sum_{r}^{B} \sum_{s}^{A} (C_r C_s)^2 \times (\text{sign of } C_r C_s S_{rs}) \right] \times \text{Fn.}(AB)$$

Rotationally invariant

We now have difficulty in defining a suitable function, Fn.(AB). But now the answer becomes obvious - break down the total energy into 1- and 2- (and in ab initio calculations, 3- and 4-) centre terms.

3. Energy Breakdowns.

(a) Total Energies.

The major advantage of breaking down the total energy, as the first step of analysis, is that it enables one to determine exactly which

* Bader (1973, 1975) has developed an alternative method of spatially partitioning the molecular charge distributions and energies of simple molecules, based on the Virial theorem. This method divides a total system into sub systems, each of which is self-contained (quantum mechanically). The constancy in properties of bonded fragments in different systems is seen to be reflected in the constancy in their charge distributions and virials.

Clementi (1967) attempted an energy analysis of ab initio calculations along the lines suggested here, for a variety of molecules and several reactions. His analyses and conclusions show the validity and strengths of such an approach.

changes are responsible for the stabilisation of a species. It is only when this has been achieved, that one can investigate with confidence, which orbitals etc. are the dominating ones concerned and then study which indices are appropriate. It will also be observed that the energy breakdown helps to illuminate changes which might otherwise be missed and in some cases leads to a conclusion opposite to that which would have been obtained by a superficial study of the results (see the analysis of $CH_5^{\oplus}$ below).

A means for partitioning the total energy was developed for use with the MINDO method. This had been previously done by Dewar (1971a) but for different purposes. Dewar's method was itself based on the energy partitioning analysis of Fischer and Kohlmar (1970), which was derived for use with the CNDO method.

The required manipulation of the energy matrix elements is as follows,

$$\text{Total MINDO energy} = \sum_r \sum_s \tfrac{1}{2} P_{rs} (F_{rs} + H_{rs}) + \text{Nuclear-Nuclear terms.}$$

The meanings of, and the explicit expressions for, F_{rs} and H_{rs} have been given previously (see Chapter 2). All that is required is that the elements of F^{AA} (and H^{AA}) which involve 1 atomic orbital, but 2 atomic centres, be transferred to E_{AB} (i.e. $\sum_{B \neq A} (Q_B - C_B) \cdot \gamma_{AB}$ transferred from E_A to E_{AB}). Also the nuclear-nuclear terms are included in the appropriate E_{AB} terms. Thus the total energy is partitioned into a matrix of E_A and E_{AB} terms. Note for an ab initio breakdown, E_{ABC} and E_{ABCD} would also be required. However these matrices would be small, involving as they do three and four centre terms. Their importance could be checked by comparing the difference in the 1-centre and 2-centre terms between two possible intermediates, with the difference in their total energies.

(b) Orbital Energies.

We have now reached something of a paradox in our proposed analysis. On the one hand we have a method of locating exactly (with respect to the method of calculation) the source(s) of stabilisation in a preferred intermediate. On the other hand we now cannot relate this stabilisation to a particular orbital or electron. This is caused by the fact that the total energy contains the nuclear-nuclear terms which cannot be partitioned between the various electrons or orbitals. So now one asks the question - how can theoretical explanations which involve the concepts of orbital symmetry, HOMO-LUMO interactions etc., be applied to methods in which nuclear-nuclear terms are explicitly calculated?

Fortunately an empirical solution is at hand for which, as yet, no satisfactory explanation has been given. The solution relies on the observed parallel variation of the total energy and components of the total energy which can be related to individual electrons and orbitals.

The total energy of a closed-shell species can be expressed as

$$E_{TOTAL} = N + 2E^N + (2J-K)$$

N is the total nuclear-nuclear repulsion,

$2E^N$ is the total electron-nuclear attraction + kinetic energy,

(2J-K) is the total electron-electron repulsion.

Therefore: $$\frac{\partial E}{\partial q_i} = \frac{\partial N}{\partial q_i} + \frac{2\partial E^N}{\partial q_i} + \frac{\partial(2J-K)}{\partial q_i}$$

Now on bringing the atomic centres in a molecule closer, N and (2J-K) change by large destabilising amounts, and E^N changes by large stabilising amounts, while the overall energy difference may only be <1% of any one of these changes. In other words there is a fine balancing of these three sets of forces. The important point is that it has been found, by Allen et al. (1967), that the changes in N and one set of E^N roughly cancel out, in relation to the other two sets of terms,

$$\text{i.e.} \quad \left| \frac{\partial E^N}{\partial q_i} + \frac{\partial (2J-K)}{\partial q_i} \right| > \left| \frac{\partial N}{\partial q_i} \cdot + \frac{\partial E^N}{\partial q_i} \right|$$

and hence the change in $(E^N + (2J-K))$ parallels the total energy change to a first approximation. Now $E^N + (2J-K)$ is the sum of the eigenvalues (S.C.F. orbital energies) of each pair of filled orbitals (not of each filled orbital). Thus the sum of the S.C.F. orbital energies may be taken as an approximation to the total energy. But more importantly, Allen found that each individual orbital energy $e^{S.C.F.}$, changed by small amounts and in the way that would be predicted from the form of the orbital involved, by consideration of its nodal properties. This is not the case with e^N, the 1-electron core orbital energy, which always becomes more stable as atom centres are brought closer. Hence the $e^{S.C.F.}$'s and their sum, $E^{S.C.F.}$ can be used for comparison of alternative conformations.

The expression for an S.C.F. orbital energy is given by,

$$e_i^{S.C.F.} = \tfrac{1}{2} \sum_r^{(i)} \sum_s^{(i)} C_r C_s \cdot F_{rs}$$

Thus each orbital can be further split up into 1 atomic orbital ($r = s$) and 2 atomic orbital ($r \neq s$) contributions. Similarly by replacing

C_rC_s by P_{rs}, we may break down $E^{S.C.F.}$ into 1 atomic orbital ($r = s$, in P_{rs}) and 2 atomic orbital terms. (N.B. These are not 'pure' 1 and 2 atomic orbital terms, since F matrix elements contain J and K terms which involve all atomic orbtials in other molecular orbitals, but with respect to the m.o. being analysed they are 'pure'.)

In comparing two intermediates, the various matrices are produced, be they bond order, energy, orbital S.C.F. energy etc., and one matrix is subtracted from the corresponding one for the other species. Now it is generally the case that several of the resulting matrix elements are much larger than the total matrix difference. Thus even now the total difference involves the balancing of several competing forces in a molecule, which is not surprising. However, although the total energy difference etc. is not necessarily 100% accurate, one can still obtain reliable information about these competing forces involved on altering the conformation. For example whether it is one or multicentre terms that are decisive, whether non-bonding interactions play a significant part and so on.

With the above as a theoretical framework for discussion, we will now return to a consideration of the results obtained. Each model or related series of models will be discussed separately. It must also be remembered that in all cases, the ab initio calculations will provide a means of checking the validity of only the broader implications and conclusions derived from the OPTMO studies, because of the practical limitations on them.

4. Simple models for S_N2 and S_E2 reactions.

As has been noted, $CH_5^{\oplus}$ and $CH_5^{\ominus}$ are simple models for the S_E2 and S_N2 reactions. In terms of the HMO theory, they represent examples of 3-atom, 2-electron and 3-atom, 4-electron systems respectively.

(a) $CH_5^{\oplus}$

Details of the previous major ab initio calculations and relative energies of various conformations have already been given. The first attempt at performing calculations on this sytem highlighted the dangers both of not optimising the geometry and also the sensitivity of relative energies to changes in the basis set, when ab initio calculations are involved. ATMOL calculations were carried out using the best optimised geometry of Dyczmons (1970) et al., (i.e. optimised with respect to their basis set). The relative energies of various conformations are given in Table 3.1. As can be seen, one observes a complete reversal in energies!

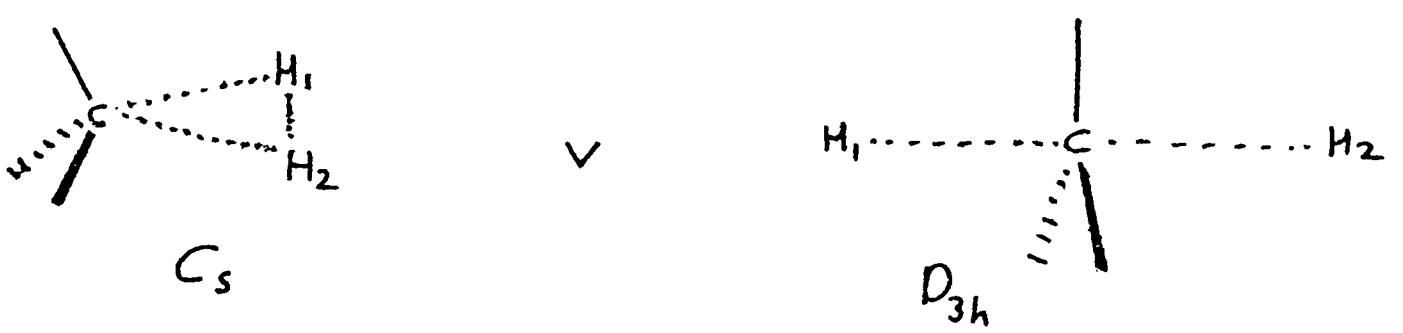
OLDMINDO calculations were also carried out using the Dyczmon's geometry. In this case it was necessary to add 0.1 Å to the C-H bond lengths, as it was found by Dewar (1972) that MINDO/2 consistently predicted C-H and N-H bond lengths to be 0.1 Å longer than their experimental values and for similar reasons O-H bond lengths must be increased by 0.15 Å if optimisation is not being performed. When it was available, OPTMO was used to obtain the equilibrium geometries and relative energies of the three species. The results are given in Table 3.1, together with details of the recently published work of Dewar (1975) on $CH_5^{\oplus}$.

In all cases the C_s species is predicted to be the most stable, but the energy difference between C_s and D_{3h} is more pronounced in the

$CH_5^{\oplus}$

	C_s	C_{4V}	D_{3h}
Dyczmons (1970)	0	6·9	14·6
ATMOL (Dyczmons geometry)	22·4	0·04	0
Pople (1972)	0	—	16·0
OLDMINDO	0	17·7	25·5
OPTMO	0	25·4	34·4
MINDO/3, Dewar (1975)	0	>0	>0

Table 3.1 Calculated Relative Energies (Kcal/mole), of $CH_5^{\oplus}$ Conformations.



C_s D_{3h}

$E(C_s - D_{3h})$ — all energies are in atomic units.

	C	H_1	H_2
H_2	0·263	−0·450	−0·044
H_1	0·263	−0·044	
C	−0·037		

(negative sign implies a more stable interaction in the C_s geometry)

Total energy difference. = −0·057

Sum of above matrix. = −0·049

Sum of all 1-centre terms. = −0·120

Sum of above 1-centre terms. = −0·125

Sum of all 2-centre terms. = +0·063

Sum of above 2-centre terms. = +0·076

Figure 3.3 Energy Difference Matrix (C_s-D_{3h}) and Analysis for $CH_5^{\oplus}$.

OPTMO calculations. However there is no experimental method for determining this difference. The final OPTMO geometries for the three conformations are given in Appendix 2 (numbers 1,2 and 3), as are all OPTMO-derived optimised geometries. Calculations by Pople (1971) were repeated using the GAUSSIAN 70 STO - 3G basis set, to produce results that could be compared with those from OPTMO.

Before attempting to discover the reasons for the preferred stabilisation of the C_s intermediate, it is worthwhile remembering the explanations previously given. The Mulder explanation is that it is due to the presence of a 3-centre, 2-electron bond between the carbon and the two hydrogens, and the HMO theory ascribes the stability to the hydrogen-hydrogen bond. The C_s-D_{3h} energy difference matrix will be studied in the first instance. The major energy differences involve the carbon and the incoming and leaving hydrogens (H_1 and H_2). The energy difference matrix elements relating to these three centres are given in Figure 3.3 (i.e. the numbers obtained when the 1-centre and 2-centre energy terms, associated with these centres in the D_{3h} conformation, are subtracted from the corresponding ones in the C_s conformation). Note that there are other 2-centre difference terms, not shown, of comparable magnitude to the 1-centre difference terms, but it is generally the case that $\Delta E_A < \Delta E_{AB}$ and only the major terms of each set are given. Taking into account all the figures, one sees that the matrix given can be said to represent all the important changes occurring on going from one conformation to the other.

This energy difference matrix may be described in three ways.

① The H-H bond is the major stabilisation term for the C_s model.

② The 1- and 2- centre difference terms associated with the C, H_1 and H_2 atoms are dominant and the rest effectively cancel out.

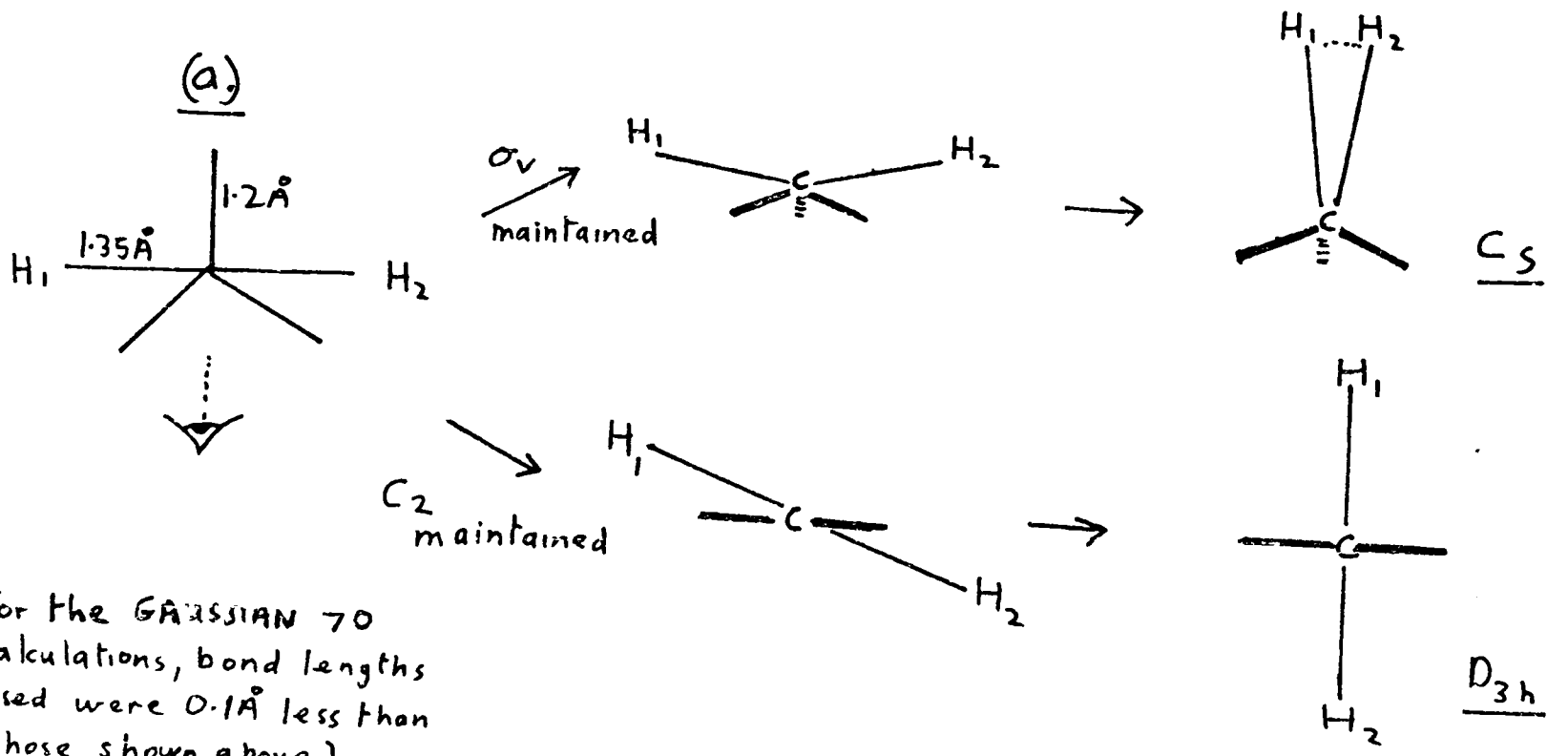
③ The 1-centre difference terms are the decisive set.

① is the HMO explanation and ② is the Mulder explanation, assuming that the 3-centre, 2-electron bond stabilises the three centres involved. However ③ is more intriguing and no such simple explanation can be elucidated at first sight. In order to study this further, the breakdown matrices of $E^{S.C.F.}$'s for the C_s and D_{3h} models, into 1- and 2- atomic orbital terms, were subtracted from each other. When this had been done it was found that the major 2-atomic orbital term favouring C_s was the $H^1_{1s}....H^2_{1s}$ term and major 1-atomic orbital terms were the H^1_{1s}, H^2_{1s} and C_{2s} terms. This suggests that there is more s character at these three centres in the C_s species. Both ab initio and OPTMO calculations show that this is true, as is given in Table 3.2. However the changes at the carbon show that while the s character does increase from D_{3h} to C_{4v} to C_s, the total electron density decreases, i.e. although the number of electrons decreases, because they are more firmly held the energy increases. Thus here is an example in which a superficial observation would lead to the the wrong conclusion, namely that the carbon contributes less to the total energy in the C_s conformation, because there are less electrons present.

But where is this 2s and 1s character coming from? To discover this one may either compare the wave functions of the D_{3h} and C_s geometries or one may observe the processes whereby these two conformations can be formed. By the latter I mean the equivalent of observing the changes in butadiene orbitals as one proceeds towards the con and dis transition states for the formation of cyclobutene, as we have described previously. The first approach has been used most successfully in determining the areas of stabilisation in the C_s molecule and the second approach will now be used to determine the origin of stabilisation.

	C_s	C_{4V}	D_{3h}
OPTMO			
H_1, electron density.	0·87	0·80	0·73
C, Total electron density.	3·665	3·953	4·022
C, 2s electron density.	1·151	0·985	0·940
GAUSSIAN 70 (Mulliken analysis).			
H_1, electron density.	0·780	0·684	0·618
C, Total electron density.	6·160	6·470	6·518
C, 2s electron density.	1·305	1·244	1·231

Table 3.2 Electron Densities in Conformations of $CH_5^{\oplus}$



(For the GAUSSIAN 70 calculations, bond lengths used were 0·1Å less than those shown above.)

The diagrams show the way in which the flat model (a.) can be distorted to give, finally, the two intermediates. The distorted forms are drawn as they would appear, if one were looking from the direction shown in (a). In the actual distortions performed, only H_1 and H_2 are moved.

Figure 3.4 'Model Reactions' of A Flat $CH_5^{\oplus}$ Model.

However, unlike the butadiene-cyclobutene reaction, we do not have reaction pathways that maintain elements of symmetry, in order that we may classify the orbitals accordingly etc.. But since we are only interested in why the transition states/intermediates differ and not the reactants, another approach is to set up a symmetrical model which can be converted into both intermediates, via symmetrical pathways.

In the case of $CH_5^{\oplus}$, such a model reaction is given in Figure 3.4. The totally flat species can be converted by movements of the two hydrogens shown, preserving different symmetry elements, into either intermediate. In the flat species we have separation of the molecular orbitals into σ and π orbitals. We can consider a small perturbation along the reaction pathways to the two intermediates. This will allow the old m.o.s to mix. Now the nine m.o.s of the flat $CH_5^{\oplus}$ are given (as derived from the MINDO and ab initio calculations) in Figure 3.5, together with MINDO eigenvalues and symmetries with respect to the relevant symmetry elements. One point that should be noted is that the HOMO is the carbon 2_p orbital out of the molecular plane. This orbital therefore contains 2 electrons in the flat model. Now we know, from the calculations on the intermediates, the occupancy of this atomic orbital in the C_s and D_{3h} models. These figures are given in Table 3.3. One observes large depopulation of this a.o. relative to the flat model, the greater depopulation being in the C_s intermediate. Thus we may deduce that on perturbing the flat model, this π-HOMO begins to mix with the UMO(s) (unoccupied m.o.s) and becomes depopulated.

In order to study this perturbation, MINDO/2 calculations were performed on two distorted geometries. In one, hydrogens 1 and 2 were raised above the plane by 0.1 a.u. (a distortion on the path

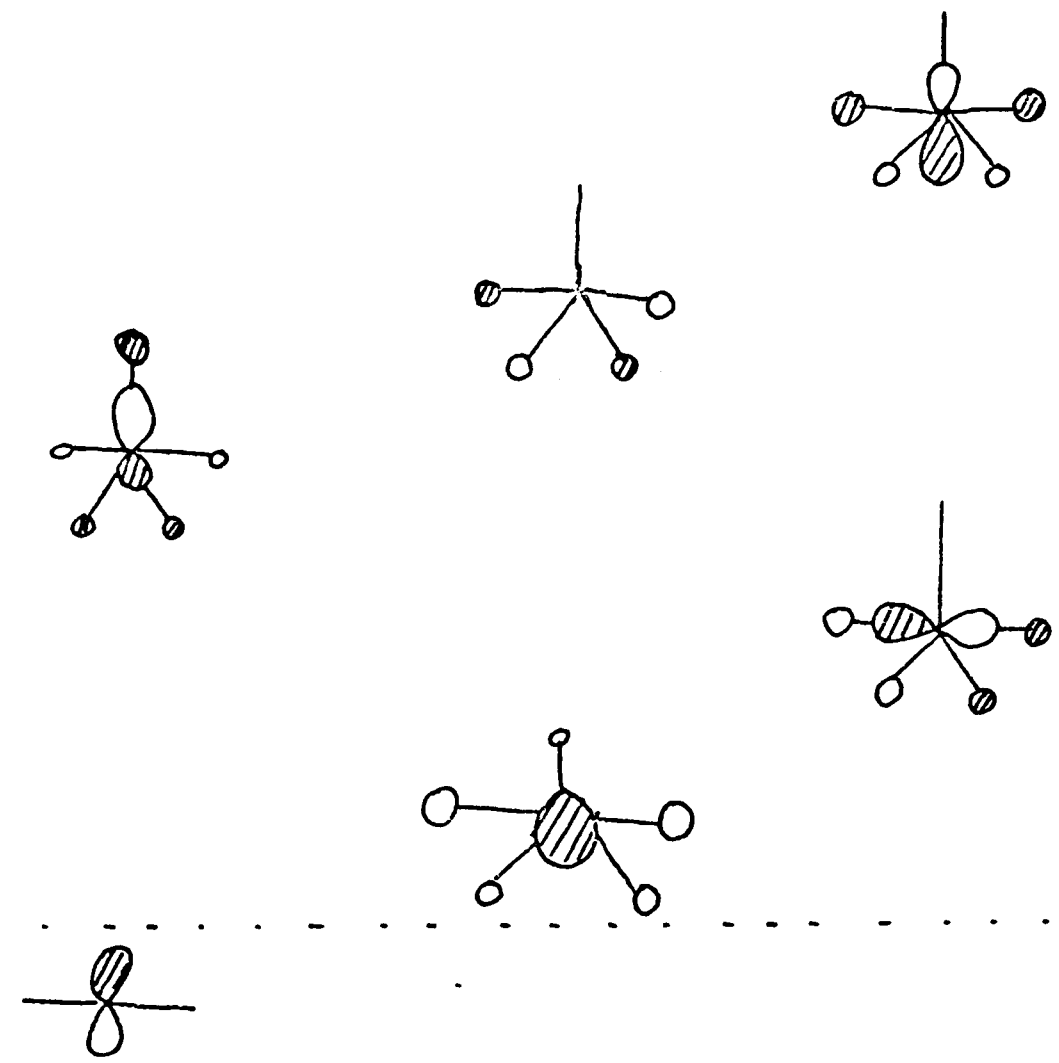


Figure 3.5 Details of the MOs of The Flat $CH_5^{\oplus}$ Model.

	Flat	C_s	D_{3h}
Electron density in π atomic orbital ($2p_z$), MINDO/2	2·0	0·34	0·98
Mulliken population analysis C_{2p_z}, GAUSSIAN 70	2·0	~0·7	1·09

Table 3.3 π-Orbital Populations in $CH_5^{\oplus}$ species.

towards C_s). In the other, one hydrogen was raised and the other lowered (a distortion towards D_{3h}) by the same amount as in the former instance. We now have new m.o.s made up of new amounts of the a.o.s on the various atomic centres. To help us analyse the geometry perturbations, we may consider the changes to occur in two stages. Firstly the old m.o.s are maintained, as the atomic centres (in this case the two hydrogens) are moved. This leads to a perturbation of the Hamiltonian and the old orbitals mix to form the new m.o.s. Now these new m.o.s can obviously be expanded in terms of the old m.o.s (in the new atomic positions). Because of the normalisation properties of MINDO orbitals (and this <u>does not apply to ab initio m.o.s</u>) the contribution C_{ijo}, from an old m.o. , ϕ_{jo}, to a new m.o., ϕ_i, is given by the simple expression,

$$C_{ijo} = \sum_r C_{i\,r} \cdot C_{jo\,r}$$

where C_{ir} and C_{jor} are the coefficients of atomic orbital Xr, in molecular orbitals ϕ_i and ϕ_{jo}, respectively,

(See Appendix 3 (a), for more detailed treatment.)

It is obviously the case that mixing will occur within the filled and unfilled sets of orbitals, as well as between filled and unfilled m.o.s. This means that the new m.o.s will contain varying amounts of all the old m.o.s, subject to symmetry considerations. However initially we will be interested in the total amount of an old m.o. in all the <u>filled</u> new m.o.s. In terms of the electron density in an old m.o. which makes up the new m.o.s , we may write

$$P_{jo} = \sum_i^{\text{filled}} P_{ijo} = \sum_i^{\text{filled}} (C_{ijo})^2$$

Where P_{jo} is the electron density and the summation is over all filled new m.o.s. (Note the actual electron population is 2 P_{jo} as there are two m.o.s with α and β spins). In other words one squares and adds up all the contributions from $\emptyset_{jo}$ in all the new filled m.o.s. This has been done for the two distortions mentioned and the results are given in Table 3.4, together with the matrix of values for C_{ijo}.

Three things are immediately apparent. The different distortions allow mixing only between orbitals of the same symmetry with respect to the symmetry element maintained during the distortion. Thus in the first case only orbitals 5,7 and 9 can mix with the HOMO π and in the other example, orbitals 6 and 8 interact with the π m.o. . Secondly, as we predicted, HOMO-UMO interactions are overwhelmingly preferred (>99.9% of electron transfer is from the HOMO in both distortions) and the other three filled m.o.s are essentially unchanged. Thirdly, there is an exceptionally large mixing between the HOMO and the LUMO in the C_s distortion (almost 10 times the electron transfer of any other interaction). HOMO-LUMO mixing is forbidden in the D_{3h} distortion. However before studying this change in any further detail we must introduce the basic elements of perturbation theory. This is required for two reasons. Firstly, to create a theoretical framework in which to place these observed changes and secondly to determine whether these changes are decisive. To elaborate this latter point it is necessary to recall how we envisaged this distortion taking place. The old m.o.s are moved and then allowed to mix. However the movement of the m.o.s themselves produces an energy change besides that associated with any HOMO-LUMO mixing. Only perturbation theory can encompass all these effects.

(a.) Distortion Towards C_{s} :-

C_{ijo}	i (new m.o.s) →	1	2	3	4	5	6	7	8	9
	e_i →	-1.53422112	-1.03759726	-0.77249029	-0.61779177	-0.33015012	-0.17474221	-0.14394783	-0.07533684	-0.06777056
j_o ↓	1	0.99977203	0.00000441	0.11411184	-0.05733004	0.00080457	0.00000048	-0.00317046	0.00000002	-0.00129941
	2	0.00311001	0.99999995	0.00111288	0.00133333	0.00000001	-0.00032015	0.00000000	-0.00001113	0.00000001
	3 (old m.o.s)	-0.00013754	0.00000004	0.99933535	0.00147617	-0.00011777	0.00000018	-0.00026343	0.00000000	0.00012737
	4	0.00737943	0.00133008	-0.00147[illegible]45	[illegible]	-0.00212272	0.00000004	0.00287145	0.00000000	0.01324385
	5	-0.02354762	0.00000000	-0.00031[illegible]22	[illegible]	0.99861355	0.00000000	-0.00000822	0.00000000	0.00035034
	6	0.00000001	-0.00132[illegible]	0.00111[illegible]	[illegible]	0.00000000	-0.00000000	0.00000000	-0.00024013	0.00000000
	7	-0.00111251	0.00000010	-0.00136295	[illegible]	-0.00112[illegible]	0.00000000	-0.00000000	0.00000000	-0.00045035
	8	0.00000001	-0.00001[illegible]	0.00000000	[illegible]	0.00000000	0.00000000	0.00000000	-0.00000000	0.00000000
	9	0.00012092	0.00000000	-0.00013445	[illegible]	0.00000000	0.00000000	-0.00000000	0.00000000	0.99998255
P_{jo}		0.99979925	0.99999991	0.99999987	0.99548783	0.00054844	0.00000018	0.00000020	0.00000000	0.00023[illegible]
	j_o →	1	2	3	4 HOMO π	5 LUMO σ*	6	7	8	9

(b.) Distortion Towards D_{3h} :-

C_{ijo}	i	1	2	3	4	5	6	7	8	9
	e_i	-1.53400243	-1.03763454	-0.77222188	-0.61767325	-0.33004091	-0.17443412	-0.14374458	-0.07522[illegible]	-0.06742245
	1	-0.99979993	-0.00000172	0.00112[illegible]27	0.00132289	0.00029065	0.00000411	-0.00[illegible]9143	-0.00[illegible]	-0.00115192
	2	0.00000092	-0.99999995	0.00111[illegible]51	0.00[illegible]14[illegible]3	0.00000037	0.00000455	-0.00000[illegible]35	-0.00001[illegible]13	0.00000055
	3 j_o	0.00132[illegible]	0.00000[illegible]71	0.99999995	-0.00[illegible]41134	0.00001[illegible]56	0.00000[illegible]51	-0.00000[illegible]	0.00000[illegible]52	0.00001025
	4	0.00000[illegible]4	0.00[illegible]94[illegible]5	0.00000[illegible]25	0.99952[illegible]4	0.00002[illegible]14	0.00[illegible]66[illegible]3	-0.00011[illegible]46	-0.00[illegible]27	0.00001[illegible]3
	5	-0.00000[illegible]27	0.00000[illegible]38	-0.00000[illegible]63	-0.00[illegible]22	0.99992[illegible]45	0.00000[illegible]49	0.00000[illegible]37	0.00000[illegible]19	0.00001[illegible]19
	6	0.00000[illegible]	-0.00000[illegible]41	-0.00[illegible]7[illegible]	-0.00[illegible]22	0.00000[illegible]16	1.00000[illegible]31	-0.00000[illegible]8	-0.00000[illegible]5	0.00000[illegible]42
	7	-0.00001523[illegible]	-0.00000[illegible]43	-0.00[illegible]1[illegible]7	-0.00[illegible]1[illegible]2	-0.00001[illegible]44	-0.00000[illegible]15	0.00015[illegible]31	-0.00000[illegible]17	0.99999[illegible]7
P_{jo}		0.99979993	0.99999991	0.99999995	0.99952[illegible]3	0.00002[illegible]24	0.00000[illegible]91	0.00000[illegible]02	0.00000[illegible]03	0.00001[illegible]42
	j_o	1	2	3	4 HOMO π	5 LUMO σ*	6	7	8	9

Table 3.4 $CH_5^{\oplus}$; Matrix of Values for C_{ijo} and P_{jo}, for Distortions Towards C_s and D_{3h} Geometries.

For the unperturbed system,

$$H^o \cdot \phi_{io} = e_i^o \cdot \phi_{io}$$

In the perturbed system,

$$H \cdot \phi_i = e_i \cdot \phi_i \text{ , where } H = H^o + H' \text{ (the perturbation)}$$

The new m.o.s and energies are then expanded in terms of the old m.o.s or in our case, in terms of the old m.o.s in the new positions. In fact for this method of perturbation (effectively a change in the overlap matrix, leading to a change in the Hamiltonian), the standard perturbation equations do not generally apply. However, again because of normalisation properties of MINDO m.o.s , in their case (but <u>not</u> for a.i. wavefunctions), the standard equations do hold (see Appendix 3(b) for more detailed explanation).

The first order correction to the energy, e_i' , of an m.o. is then given by, (see Murrell et al. (1965)).

$$e_i' = H_{ii}', \quad \left(H_{ii}' = \int \phi_{io} \cdot H' \cdot \phi_{io} \, d\tau\right)$$

- the interaction of the old m.o. with the perturbation. In terms of our distortion, this corresponds to the change in the energy of the old m.o. ϕ_{io}, as it moves to the new position, an <u>intra</u>— m.o. change.

The first order coefficients of mixing are given by

$$C_{ijo} = \frac{H'_{iojo}}{e_i^o - e_j^o} \quad , \qquad \left(\phi_i = \phi_{io} + \sum_{io \neq jo} C_{ijo} \cdot \phi_{jo} + \ldots\right)$$

Thus the mixing varies inversely with the energy gap between the orbitals that interact, and directly with the interaction between them, due to the perturbation. The overlap between the old m.o.s, ϕ_{io} and ϕ_{jo},

in the new environment, is considered to be a guide to the value of H'_{iojo}, in the type of perturbation being considered.

The second order energy change associated with these inter-m.o. effects is given by

$$\underline{e_i}'' = \sum_{i \neq j} \frac{|H'_{iojo}|^2}{e_i^o - e_j^o} = \frac{\sum_{i \neq j} (C_{ijo})^2 . (e_i^o - e_j^o)}{\left(= \sum_{i \neq j} P_{ijo} (e_i^o - e_j^o)\right)}$$

We have now achieved our purpose in obtaining expressions for the energy changes we actually calculate and in particular in breaking down these changes in accordance with our view of how they can be considered to occur.

We will first determine whether the energy difference between 'Cs' and 'D_{3h}' distortions of the flat species arises from first order (intra-m.o.) or second order (inter-m.o.) effects. As we are discussing orbitals, we will observe the change in $E^{S.C.F.}$ (i.e. the sum of the orbital energies/eigenvalues of each pair of filled orbitals - see section 3(b)) as well as in E_{TOTAL}, the total energy. The relative values of these energies are given in Table 3.5 and both show the greater stability of the 'Cs' distorted geometry.

The second order perturbation energies for particular interactions are given in the Table and were calculated from the expression,

$$e''_{ijo} = (C_{ijo})^2 . (e_i^o - e_j^o) = P_{ijo} . (e_i^o - e_j^o)$$

using the values for C_{ijo} derived as described previously, and values for e_i^o's from the flat calculation.

(Note it is here that we assume that the perturbation is small enough to ignore second order coefficient changes and higher order terms - perfectly reasonable in the case being considered).

	Energies for 'C$_s$' distortion, (a.u.).	Energies for 'D$_{3h}$' distortion, (a.u.).
ΔE_{TOTAL} (relative)	0	0.000319
$\Delta E^{S.C.F.}$ (relative)	0	0.000608
$(= \sum_i \Delta e_i^{S.C.F.}$, i = Filled pairs of electrons)		
$e''_{4,5 \leftarrow j_0}$	−0.001108	0
$e''_{4,6}$	0	−0.000154
$e''_{4,7}$	−0.000204	0
$e''_{4,8}$	0	−0.000176
$e''_{4,9}$	−0.000129	0
e''_{TOTAL}	−0.001441	−0.000330
$\Delta e''_{TOTAL}$ (relative)	0	0.001111
$\therefore$ $\Delta e'_{TOTAL}$ (relative)	0.000503	0

$(\Delta e'_{TOTAL} + \Delta e''_{TOTAL} = \Delta E^{S.C.F.})$

Table 3.5 Energetics of the 'C$_s$' and D$_{3h}$' Distortions, For Flat $CH_5^{\oplus}$.

However it may be suggested that all interactions of form e''_{ijo}, should be determined besides those between the HOMO (4) and all the UMO'S (5,6,7,8 and 9). This is not necessary for the following reasons. Firstly, the interactions between unfilled orbitals do not affect the energy simply because those orbitals are never filled and hence cannot contribute to the total energy expression. Secondly, interactions between filled orbitals also do not affect the total energy since the energy gained by one m.o. is lost from the other. This is so because the two related energy terms differ only in the sign of $(e_i^o - e_j^o)$. Finally, we have interactions between the UMO'S and other filled orbitals besides the HOMO π. But we have seen that > 99.9% of all electron transfer from filled to unfilled m.o.s occurs from the HOMO π and we may therefore discount these interactions also (we will study this observation in more detail later). Hence only HOMO-UMO second order energy changes need be calculated to obtain the <u>total</u> second order perturbation energy change.

When we have calculated the HOMO-UMO interaction energy changes (see Table 3.5) we observe that the 'Cs' distorted species is strongly favoured by these second order effects and more importantly, the extra second order energy stabilisation in the 'Cs' species can be almost <u>exclusively</u> attributed to the HOMO-LUMO interaction. Also the relative second order energy stabilisation (.00111) is greater than the relative stabilisation of $E^{S.C.F.}$. (.00061) (N.B. In both cases the sum is made over all <u>pairs</u> of filled m.o.s and not over each electron. This maintains consistency and is in line with the assumption that $\sum_{i}^{(pairs)} e_i^{S.C.F.}$ rather than $\sum_{i}^{(electrons)} e_i^{S.C.F.}$, is a good representation of the total energy). However in terms of the perturbation theory, the overall $\Delta E^{S.C.F.}$ stabilisation is a sum of the first and second order contributions. This means that the first order energy change must

destabilise the C_S species, by 0.00050! We have therefore conclusively shown that it is the HOMO-LUMO interaction which stabilises the 'C_S' distorted model with respect to the 'D_{3h}' distorted model, and that this effect is larger than, and of opposite sign to, the intramolecular orbital destabilising effect.

Before leaving these particular results, it is worthwhile studying the implications of the overwhelming preference for electron transfer from the π HOMO in <u>both</u> distortions, and in particular to the LUMO in the C_S case. Electron transfer from old m.o., ϕ_{jo}, to new m.o., ϕ_i, is given by the expression,

$$P_{ijo} = (C_{ijo})^2 = \frac{(H'_{ijo})^2}{(e_i^o - e_j^o)^2}$$

Now the expression $(e_i^o - e_j^o)^2$ only varies to a small degree compared to the 1000fold or more increase in electron transfer from the π rather than σ filled orbitals. This must imply that it is the interaction term, H'_{iojo}, that is decisive. When one remembers that this term is related qualitatively to the overlap of the old m.o.s in the new positions, we can possibly understand this phenomenon. It may be attributed to the fact that the old σ and σ^* orbitals will 'see' very little of each other (in terms of overlap) on perturbing the geometry as we have done, and hence will remain virtually orthogonal with respect to the inter-m.o. Fock matrix element. Whereas much stronger 1,2 interactions will arise between the old π - 2_p orbital and the orbitals containing contributions from the perturbed hydrogen 1s a.o.s. (σ & σ^*). It will be interesting to observe what happens when several π orbitals are involved, some unfilled, as will be the case in later systems to be studied.

These considerations might explain the preference for π electron transfer but not why it occurs so strongly to the LUMO in the 'C_S'

case (obviously this is symmetry forbidden in the D_{3h} distortion). The normal explanation generally given is that the small energy gap between HOMO and LUMO favours this transfer. While this is true it cannot be the whole story. In Table 3.6. we have the amounts of the five σ and σ^* orbitals that mix (allowed by symmetry) into the HOMO in the 'C_s' distortion. We know from perturbation theory that this equals $H'_{i\phi j\phi}$/(energy gap) and we have the energy gaps from the original calculation. Therefore we can derive the values for $H'_{i\phi j\phi}$. As can be seen there are large variations in $H'_{i\phi j\phi}$ also. The values of $H'_{i\phi j\phi}$ can to some small extent be related to the coefficients of the a.σ.s on the perturbed hydrogens (C^{1s}_{H1}) in the σ orbital being considered. Thus σ orbital 3 which has a very small energy gap with the HOMO (even less than the HOMO-LUMO energy gap!), but only has a small contribution from the 1s a.σ. on hydrogens 1 and 2, does not mix in with the HOMO to any great extent. However this is not a satisfactory answer as σ^* orbital 7, also has a small value for C^{1s}_{H1}, but still has a high value for $H'_{i\phi j\phi}$. It is obvious that overlap considerations can only distinguish between gross changes (such as between $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ electron transfer) and are not quantitatively accurate as an indication of H'_{ijo}. This problem will be re-examined later, in the light of further results.

In order to ensure that the interactions we have noted for our small perturbations are related to the differences in the final intermediates, we will break down the m.o.s in the intermediates in terms of the m.o.s of the flat model. It must be remembered that the perturbation theory analysis will not now apply, but the breakdown is still valid in its own right. Also there will now be large contributions in the filled m.o.s from <u>all</u> the old m.o.s, as old m.o.s are now a poor

orbital (jo)	C_{4jo}	energy gap	$\therefore H'_{4jo}$	$C^{1s}_{H_1}$
σ 1	.0073	.917	.0067	.35
σ 3	.0048	.154	.0007	.12
σ^* 5 (LUMO)	.0620	.288	.0179	.37
σ^* 7	.0207	.474	.0098	.17
σ^* 9	.0153	.550	.0084	.45

Table 3.6 Details of π/σ Mixing For the C_s Distortion to Flat $CH_5^{\oplus}$.

representation of the new filled m.o.s and must be extensively mixed to produce them. The new matrix of C_{ijo}'s and the values for P_{jo} are given in Table 3.7. We still observe that the HOMO is much more heavily depopulated in the C_s intermediate, and simultaneously the LUMO (and other UMO's) has a greater electron population. In fact the total extra LUMO population in the C_s intermediate (.160) can be almost totally accounted for by the LUMO population in the C_s HOMO ($.381^2$ = .145), which is zero for the D_{3h} HOMO. The earlier conclusions therefore still hold.

We must now return to the reasons for this long and somewhat tortuous analysis. It had been found that 1s and 2s character on the hydrogens and the carbon atom were greater in the C_s intermediate than the D_{3h} intermediate and their origins were of interest. We observe that the major components of the LUMO of the flat model which can only be populated from the HOMO (for symmetry reasons) in the C_s distortion, are the 2_s on the carbon (coefficient, .71) and the 1s a.o.s on hydrogens 1 and 2 (coefficients, -, 37) - see Figure 3.5. These contributions can in fact account for all the major elements of the energy difference matrix (see Figure 3.3), namely, the 1-centre stabilisations on H_1,H_2 and carbon, the 2-centre stabilisation $H_1 \cdots H_2$, and the 2-centre destabilisations, C-H_1 and C-H_2, (the latter since the coefficients of a.o.s 1s (hydrogens) and 2_s (carbon) are of opposite sign).

We therefore have an explanation, in terms of HOMO-LUMO interactions which fits all the calculations and it is now necessary to test whether it is of general applicability to related reactions or whether it is peculiar to the possibly over-simple case of $CH_5^{\oplus}$. But before we study the case of $CH_5^{\ominus}$, it is necessary to return to the original bond order and Mulder explanations and re-examine them in terms of the above conclusions.

(a) MOs of the D_{3h} conformation in terms of the flat MOs.

C_{ij_0}	i	1	2	3	4	5	6	7	8	9
	e_i	-1.4099	-0.0116	-0.7702	-0.7752	-0.2498	-0.2266	-0.1527	-0.1527	-0.1377
	1	0.9933	-0.3120	-0.0151	-0.0000	0.2492	-0.0896	-0.0000	0.1591	-0.0454
	2	-0.0247	1.2278	0.2542	0.7533	-0.1059	-0.3775	-0.1306	-0.2672	0.2569
	3	-0.0873	0.0994	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.0000
j_0	4	-0.0411	0.4401	0.7245	0.0000	0.0000	-0.0000	-0.0000	0.0000	-0.0000
	5	-0.0867	-0.3193	0.0970	-0.0000	0.8414	-0.3474	0.0000	-0.1414	0.1554
	6	-0.3129	0.1271	0.1417	-0.4422	-0.0926	-0.2144	-0.6231	-0.1499	0.1240
	7	0.0212	-0.8502	1.1433	0.0000	-0.4156	-0.1488	0.0000	-0.1172	-0.2054
	8	1.0051	-0.2431	-0.2713	0.4749	0.1770	0.4229	-0.3525	0.2052	-0.2389
	9	-0.0322	-0.4395	-0.5291	-0.0000	-0.1514	-0.4563	-0.0000	0.3501	0.4172
	P_{j_0}	0.9871	0.8912	1.0235	0.5249	0.1303	0.2318	0.7597	0.3625	0.2025
	$j_0 \rightarrow$	1	2	3	4 HOMO π	5 LUMO σ*	6	7	8	9

(b) MOs of the C_s conformation in terms of the flat MOs.

C_{ij_0}	i	1	2	3	4	5	6	7	8	9
	e_i	-1.4443	-0.8774	-0.7371	-0.7913	-0.3350	-0.2137	-0.1652	-0.1042	-0.1137
	1	0.9216	0.0525	0.0047	0.1317	0.0844	-0.0045	-0.0000	0.0163	0.0413
	2	-0.0121	0.3519	-0.7876	-0.2255	-0.0249	-0.2383	-0.1421	0.2729	-0.2317
	3	-0.0004	0.2555	0.0026	0.0000	-0.4211	-0.4211	-0.0000	0.3535	0.3227
j_0	4	0.0572	-0.4055	0.1100	-0.0000	-0.7773	-0.4769	0.0000	-0.0158	0.0000
	5	-0.0511	-0.3512	0.0110	0.0000	0.0562	-0.0095	-0.0000	-0.0028	-0.1210
	6	-0.0009	0.1355	0.4332	-0.1237	-0.0139	-0.1325	-0.0000	0.1521	0.1345
	7	-0.0378	0.4295	0.0748	-0.5441	-0.2386	0.1435	-0.0124	-0.2461	-0.0276
	8	0.0132	-0.3745	-0.4233	0.2447	0.2600	0.2543	-0.5785	-0.2913	0.3222
	9	-0.0354	0.3424	-0.0312	0.2981	-0.0090	-0.3219	0.0054	-0.7600	-0.2623
	P_{j_0}	0.9374	0.7946	0.4372	1.1683	0.2963	0.2435	0.4865	0.3706	0.2052
	$j_0 \rightarrow$	1	2	3	4 HOMO π	5 LUMO σ*	6	7	8	9

Table 3.7 Breakdown of The MOs of The C_s and D_{3h} Species in Terms of The MOs of Flat $CH_5^{\oplus}$.

As was stated when the theory behind the bond order factors was elucidated, the energy change associated with the bond order factor is that derived by perturbation theory. However this is the first order energy change, summed over the filled m.o.s. In that respect there is no relation between bond order factors and explanations based upon HOMO-LUMO interactions. At the same time, the bond order factors do give the initial gradients of the energy changes associated with each m.o. on introducing the relevant resonance integral, β. In other words if one were to recalculate the Hückel m.o.s of a π-hydrocarbon with a small perturbing, β_{rs} (eg.1), present, the overall energy change would be well correlated with P_{rs}. Also the new m.o.s could be formed by mixing the old m.o.s and HOMO-UMO electron transfer would therefore be involved. Thus the value of P_{rs}, a first order term, predicts the total energy change associated with first and second order perturbations. Hence although the explanations are different, as they must be in their different contexts, they are both valid in their predictive capacities. It is nevertheless probably true to say that the HOMO-LUMO treatment is more appropriate to the physical reality, in that the intermediates differ in the degrees and nature of electron redistribution rather than in static properties of the same molecular orbitals. Similarly the Mulder explanation is a first order explanation, in terms of a 3-centre, 2-electron bond, which would not account for the increased 2_s electron density at the carbon. Again it is the right prediction, but for the wrong reasons, in terms of our analysis.

(b) $\underline{CH_5^{\ominus}}$

Again the energies of D_{3h}, C_{4v} and C_s species were required. In

this case, two conformations of C_s symmetry may be of interest, namely with $H_1.....H_2$ eclipsed or staggered in relation to one of the other hydrogens. This did not apply for $CH_5^{\oplus}$ as there was found to be virtually free rotation between these two forms. Initially the ab initio optimised geometry of Mulder was employed (+0.1Å for C-H bond lengths). The relative energies are given in Table 3.8 and it is seen that D_{3h} is by far the most stable species. Taking into account the accuracy of the OLDMINDO results for $CH_5^{\oplus}$, based on ab initio optimised geometries (rather than the ATMOL results - see Table 3.1), this alone might be considered sufficient evidence for the preference for the D_{3h} species, using MINDO/2 calculations.

It is obviously desirable to derive optimised geometries using OPTMO. This led to certain problems. Although the D_{3h} species optimised with ease, as one might intuitively expect if it is the most stable form, and the C_{4v} model did so relatively easily (see below), the C_s (staggered and eclipsed) forms were not so inclined. Either the S.C.F. cycling would not converge, itself an indication of instability, and for which there is little remedy within OPTMO, or the species lost its C_s symmetry. This might seem to be a paradox as the input species is supposed to retain its symmetry in the OPTMO program. However if large destabilising forces are present, which is quite likely for the C_s transition state, a small deviation from symmetry in the last decimal place of a Cartesian coordinate will rapidly lead to gross distortions of the molecule after a small number of up-datings of the coordinate matrix. It is even possible that no stationary point of C_s symmetry exists on the potential energy surface. A similar problem occurred with the C_{4v} species and it was not possible to achieve the 'total' optimisation desired.

CH_5^-

	C_s (staggered)	C_{4v}	D_{3h}
Mulder (1970)	54·5	54·5	0
OLDMINDO	64·1	35·0	0
OPTMO	?	>0	0*

(* Optimised bond lengths, used for the flat model, were as follows, C–H$_1$ 1·52Å, C–H$_3$ 1·2Å)

Table 3.8 Calculated Relative Energies (Kcal/mole), of $CH_5^{\ominus}$ Conformations.

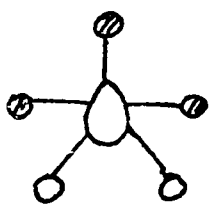
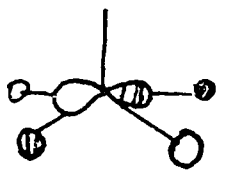
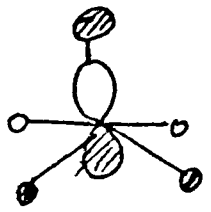
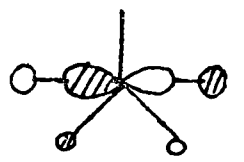
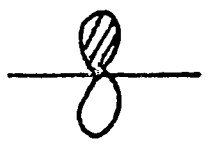
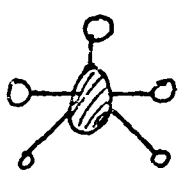
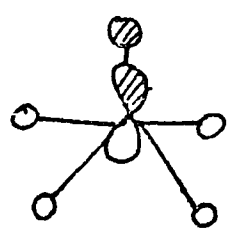
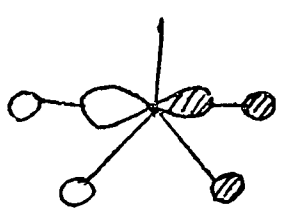
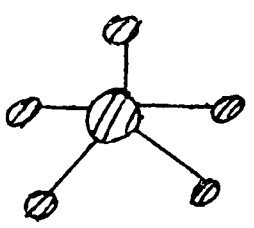
		Symmetry with respect to σ_v	Symmetry with respect to C_2	$e^{S.C.F.}_{MINDO}$
9		+	σ^* +	0·516
8		−	σ^* −	0·497
7		+	σ^* +	0·441
(LuMo) 6		−	σ^* −	0·420
(HOMO) 5		+	π −	0·026
4		+	σ +	−0·013
3		+	σ +	−0·183
2		−	σ −	−0·451
1		+	σ +	−0·882

Figure 3.6 Details of the MOs of The Flat $CH_5^{\ominus}$ Model.

(A note on optimisation might be in order here. A gradient restriction of 10^{-3} hartree/bohr on all varying x,y and z energy gradient matrix elements was found to be sufficient to optimise bond lengths well and bond angles quite well. However a gradient restriction of 10^{-4} hartree/bohr was required to give accurate dihedral angles and was used in almost all calculations. The latter process is rather slow as the atoms can only rotate by a small angle each cycle. This has since been remedied apparently by Dewar (1975b), who uses the internal coordinates of the molecule rather than Cartesian coordinates to define the gradient energy matrix).

The OPTMO geometry of the D_{3h} system is given in Appendix 2 (number 4) and is in good agreement with the ab initio-derived geometry of Mulder, taking into account the lengthening of C-H bonds by MINDO/2.

Because of the difficulties encountered with $CH_5^{\ominus}$, it was thought that a more suitable species to be studied by OPTMO would be the dihydroxy anion - $CH_3(OH)_2^{\ominus}$. Also this is a more chemically realistic model. However here again, although it was possible to derive a T.S. of D_{3h} symmetry, no C_s species could be likewise located.

Despite these problems, we can still analyse a flat $CH_5^{\ominus}$ model and investigate the changes brought about by the addition of two electrons to $CH_5^{\oplus}$. The C-H bond lengths used in the flat species were those found by the OPTMO calculations on the D_{3h} ($CH_5^{\ominus}$) geometry and are given in Table 3.8. The flat species was distorted in exactly the same ways as described for $CH_5^{\oplus}$ and the new m.o.s were expanded in terms of the old m.o.s. The nine flat MINDO/2 m.o.s of $CH_5^{\ominus}$ are shown in Figure 3.6. They are qualitatively the same m.o.s as those of $CH_5^{\oplus}$, and now the orbital which was the σ^* LUMO (see Figure 3.5)

is filled. However the MINDO ordering changes slightly, in that the π orbital is still the HOMO (although GAUSSIAN 70 calculations that were done, suggest that the order in $CH_5^{\oplus}$ is preserved in $CH_5^{\ominus}$ with the π being the (HOMO-1) orbital - this will not affect the subsequent discussion). The important change to note is that now the new σ^* can only mix with the HOMO π in the D_{3h} distortion.

The matrix of C_{ijo}'s and the values for P_{jo} associated with these geometry perturbations are given in Table 3.9. As before, electron transfer can only occur between orbitals of the same symmetry. Hence for C_s distortion the π HOMO mixes with orbitals 7 and 9, whilst for D_{3h} distortion it mixes with orbitals 6 and 8. As for $CH_5^{\oplus}$, we observe that > 99·9% of all electron transfer is from the HOMO π in both cases, and that in the D_{3h} — allowed mixing of π HOMO and σ^* LUMO, this interaction is of overwhelming importance. (Note that the interaction between filled orbitals 4 and 5, is very large, for the C_s distortion. These orbitals <u>were</u> the LUMO and HOMO respectively in $CH_5^{\oplus}$. Therefore this 'old' HOMO-LUMO C_s interaction of $CH_5^{\oplus}$ is still present but since both orbitals are now filled the energy contribution from the mixing is zero).

The relative values of the energies, $E^{S.C.F}$. and E_{TOTAL}, for the distorted forms are given in Table 3.10, together with the derived values for all significant second order interactions. Again, by deduction, we find that the first order perturbation energy favours the species (C_s') which is less stable overall. Also the stabilisation of the 'D_{3h}' form can be completely accounted for by the HOMO-LUMO interaction.

With the importance of the HOMO-LUMO interaction as our conclusion

(a.) Distortion Towards C_s:-

C_{ij_o}	i. 1	2	3	4	5	6	7	8	9
e_i	-0.88117689	-0.45470143	-0.18317279	-0.01328895	0.02573271	0.41917868	0.44104472	0.49673544	0.51527796
1	-0.99999828	0.00000001	0.00023177	-0.00129213	-0.00182612	0.00139022	-1.00012143	0.00000000	-0.00126671
2	0.00010004	-1.00000000	0.00000004	0.00000000	0.00000000	-0.00000941	0.00000001	-1.00000476	0.00000000
3	-1.00124442	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00041754	0.00000000	-1.00079151
4	0.00000000	0.00000000	-1.00000158	-1.00149575	0.01751763	0.00000000	0.00000000	0.00000000	-0.00252354
5 Jo	0.00118954	0.00000000	0.00012997	0.99534998	0.99990173	0.00000000	-0.00038319	0.00000000	-0.00115715
6	0.00121331	0.00000000	-0.00750124	0.01224553	-0.00155463	0.00000000	-0.01448113	0.00000000	0.00000000
7	-0.00109447	0.00000000	0.00000000	0.00000000	0.00000000	-1.00000480	0.00000000	-0.00319715	0.00000000
8	0.00111111	-1.00015149	-0.00119121	0.00158114	-0.01438765	0.00000000	0.00000378	0.00000000	-1.00176274
9	-0.00000586	0.00000000	-0.00017562	0.00145021	-0.01110854	-0.00319717	0.00000489	0.00000000	0.00000000
P_{jo}	0.99999997	1.00000001	0.99999999	0.99997958	0.99965582	0.00000001	0.00020932	0.00000000	1.00012541
Jo →	1	2	3	4	5 HOMO π	6 LUMO σ*	7	8	9

(b.) Distortion Towards D_{3h}:-

C_{ijo}	i 1	2	3	4	5	6	7	8	9
e_i	-0.88119641	-0.45470438	-0.18320599	-0.01304928	0.02534455	0.41922198	0.44095612	0.49673583	0.51564455
1	0.99999941	-0.00000341	0.00034245	0.00033135	-0.00000026	0.00000000	0.00011691	-0.00000001	-0.00000022
2	-0.00010001	-0.99999833	0.00000010	-0.00000003	0.00000000	-0.00027215	0.00000004	-0.00000457	0.00000001
3	0.00000298	-0.00000001	-0.99999984	-0.00043797	-0.00000008	0.00000001	0.00000445	-0.00000002	-0.00001933
4 Jo	0.00033112	-0.00000000	0.00013817	-0.99999952	-0.00000010	0.00000000	0.00034032	-0.00000003	-0.00000079
5	0.00000125	0.00000000	-0.00000008	-0.00000003	0.99965582	-0.00311554	0.00001552	0.00000000	0.00000195
6	-0.00000001	0.00000738	-0.00000001	0.00000015	-0.00000021	-0.99944933	0.00000054	-0.00000000	0.00000000
7	0.00011101	-0.00014001	-0.00012347	-0.00034517	0.00001552	-0.00000029	-0.99999614	-0.00000012	-0.00134557
8	0.00000001	-1.00011411	-0.00000001	0.00000002	-0.00009517	-0.00020772	-0.00000018	0.99999988	0.00000011
9	0.00000009	0.00000004	-0.00014923	-0.00000003	0.00000000	0.00000002	-0.00184522	-0.00000014	0.99999912
P_{jo}	0.99999997	0.99999941	0.99999996	0.99999933	0.99965577	1.00000001	0.00000031	0.00000001	0.00000000
Jo →	1	2	3	4	5 HOMO π	6 LUMO σ*	7	8	9

Table 3.9 $CH_5^{\oplus}$; Matrix of Values For C_{ijo} and P_{jo}, For Distortions Towards C_s and D_{3h} Geometries.

	Energies For 'Cs' distortion.	Energies For 'D3h' distortion.
ΔE_{TOTAL} (relative)	0·000109	0
$\Delta E^{S.C.F.}$ (relative)	0·000262	0
$e''_{5,6 \leftarrow j_0}$	0	−0·000432
$e''_{5,7}$	−0·000086	0
$e''_{5,8}$	0	−0·000044
$e''_{5,9}$	−0·000060	0
e''_{TOTAL}	−0·000146	−0·000476
$\Delta e''_{TOTAL}$ (relative)	0·000330	0
$\therefore \Delta e'_{TOTAL}$ (relative)	0	0·000068

Table 3.10 Energetics of the 'Cs' and 'D3h' Distortions to Flat $CH_5^{\oplus}$.

and new premise for prediction of conformational preference, we will proceed to study other, more complex systems. In each case, we will require to find and distort a flat model in the direction which maximises this (and similar) interactions.

5. Models for S_N2' and S_E2' reactions

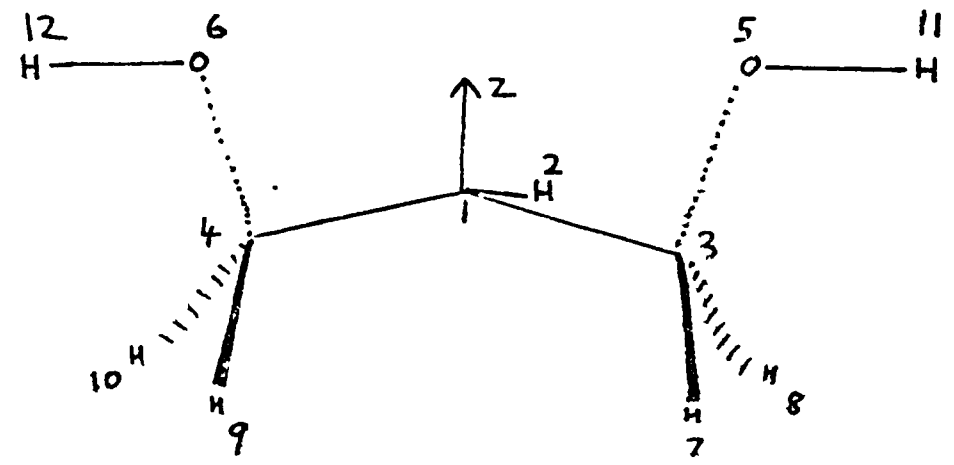
These are interesting examples for two reasons. Firstly, as in the previous reactions, the transition states may have elements of symmetry, which could aid interpretation of the factors influencing the reaction. Also the syn preference of the S_N2' reaction appears to conflict with the ideas of steric repulsion, electron correlation and eclipsed interactions which are often used to explain reaction preference.

(a) S_N2'

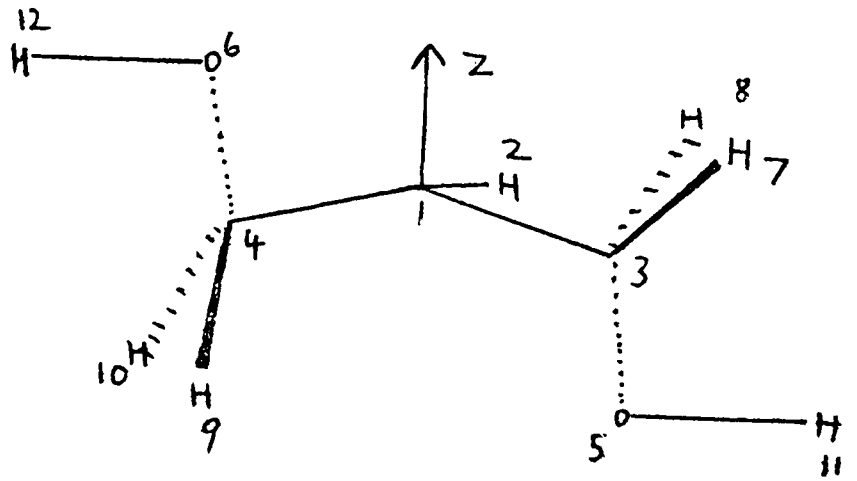
Here the model system chosen was the attack of hydroxide on allyl alcohol. Initially the symmetric syn and anti species were investigated. The input geometries were of symmetries C_s and C_2 respectively (see Figure 3.7), higher than that of the reactants together. It is a trivial exercise to show that these symmetries are both allowed for T.S.s by McIver's (1974) criteria. The energies of these models were studied by both the GAUSSIAN 70 and OPTMO methods.

OPTMO. The optimised geometries of allyl alcohol and then the syn and anti T.S.s were derived and are illustrated in Appendix 2, (numbers 5,7 and 8). The syn T.S. was also geometry-optimised while restricting the hydrogen on the central carbon to the plane formed by the three carbon atoms (as it is in the anti T.S.). This was of interest for the analysis and also in the light of certain GAUSSIAN 70 results (see below). The relative energies of the various species are given in Figure 3.7.

S_N2'



SYN (C_s).



ANTI (C_2).

Method	Reactants	ANTI Intermediate	SYN (H in C-C-C plane)	SYN (H Free)	C·····O lengths (opt)
OPTMO	60·8	2·3	1·3	0·0	~ 1·35 Å
GAUSSIAN 70	58·7	1·10	3·24	0·0	~ 1·53 Å

Figure 3.7 Input Species, and Relative Energies (Kcal/mole), of Optimised Geometries of S_N2' Models.

GAUSSIAN 70 calculations were performed on the same species as above. However as there were many variable geometrical parameters, only a limited amount of optimisation was carried out. In all cases, the bond lengths were optimised and their optimum values are given in Figure 6 of Appendix 2, together with the assumed bond angles and other details of optimisation. This is consistent with the aim of the major part of the ab initio calculations that were performed, which was to check the more general features of the semiempirical calculations rather than their fine details, for which vast, and impossible, amounts of computer time would have been required. The resulting relative energies are given in Figure 3.7.

In order to determine whether a species existed which was both non-symmetric and more stable than one/either of the symmetric species, the OPTMO syn species was deformed so that one OH group was restricted to the c-c-c plane (in both of the two possible ways) and the coordinates of the other OH group, together with those of the rest of the molecule were allowed to optimise. Note that this is analogous to Dewar's non-symmetric, non-aromatic T.S. (Figure 1.8) in forbidden pericyclic reactions and continuing the analogy, one might expect the resulting arrangement to be more stable than the anti ('forbidden') model. However, in all cases this was not found to be so and both symmetric species were more stable than the distorted form.

The calculations enable one to make some interesting and perhaps surprising observations.

1) The prediction of both sets of calculations is that hydroxide ion plus allyl alcohol is less stable than either the syn or anti species by

over 50 k.cal./mole, i.e. in the gas phase we are dealing with intermediates rather than T.S.s. It must be mentioned that, although the ab initio calculations are not fully optimised, the changes observed on variation of bond lengths show that this difference would definitely remain on total optimisation, especially since bond angle variation will have a much smaller effect than bond length variation, on the energies.

2) The ab initio calculations attribute the stability of the syn T.S. to the out of plane deformation of the central hydrogen, whereas the OPTMO results suggest that this is only a partial factor. However the ab initio results are not really accurate enough to justify this type of detailed breakdown.

3) The C....O bond lengths are much longer in the ab initio calculations on the intermediates and are probably closer to the experimental distances. Thus in all further calculations using OPTMO on this system, the calculations were repeated with the longer distances (~1.5Å), to check that the results and inferences still held. In all cases, this was found to be so.

Before studying these results, a general point must be mentioned. We have observed that with the S_E2 models and now with the S_N2^I models, we find that the optimised geometries are those of intermediates and not T.S.s. One may therefore question the relevance of these calculations, on isolated molecules, to the situations found in the chemical reactions themselves. This problem will arise in several other of our examples, and will be discussed later (see section 11).

The first step in distinguishing between the two OPTMO intermediates is to examine the differences in their (total) energy breakdowns. It will be recalled that the simple HMO theory ascribes the stability of

the syn model to a 1,5 bonding interaction, between in this case the two oxygens. However it can be seen from the total energy difference matrix (Table 3.11) that this interaction is more antibonding in the syn species and favours the anti intermediate. Again it is the 1-centre energy difference terms that strongly stabilise the syn intermediate and the 2-centre terms are of the opposite sign and strongly destabilising. The major 1-centre difference terms that favour the syn intermediate are associated with the three carbons atoms (1,3 and 4). (N.B. The large stabilising values for hydrogens 7 and 9 almost cancel out with the values for hydrogens 8 and 10, the differences between the two sets of values being due to the different dihedral angles in the two intermediates). The values for the 2_S character on the main atoms are found to be as follows.

	C_1 (central carbon)	C_3	O_5
2s electron density, SYN	1.287	1.114	1.522
2s electron density, ANTI	1.204	1.096	1.525

We see that, as with $CH_5^{\oplus}$, the three carbons possess increased 2s electron density in the syn intermediate, especially on the central carbon.

In order to discover what the effects of movement of the central hydrogen are, we have computed the energy difference matrix between the syn (H fixed, planar) and anti species (Table 3.12). It can be seen that the 1-centre energy difference terms are still determinative, while being of smaller magnitude. Also the 1-centre difference terms on all five main atoms now stabilise the syn form. We can therefore deduce that the movement of the hydrogen in the syn intermediate particularly

E (SYN-ANTI)

	1	2	3	4	5	6	7	8	9
1	[illegible]								
2	[illegible]	-1.[illegible]							
3	0.[illegible]	-0.[illegible]	[illegible]						
4	0.[illegible]	-0.[illegible]	[illegible]	[illegible]					
5	-0.[illegible]	-1.[illegible]	-1.[illegible]	-0.[illegible]	[illegible]				
6	-0.[illegible]	-0.[illegible]	-0.[illegible]	-0.[illegible]	[illegible]	[illegible]			
7	0.[illegible]	0.[illegible]	0.[illegible]	-0.[illegible]	0.[illegible]	0.[illegible]	-0.[illegible]		
8	-0.[illegible]	0.[illegible]	-0.[illegible]	0.[illegible]	-0.[illegible]	-0.[illegible]	0.[illegible]	[illegible]	
9	0.[illegible]	0.[illegible]	-0.[illegible]	0.[illegible]	0.[illegible]	0.[illegible]	0.[illegible]	-0.[illegible]	[illegible]
10	-0.[illegible]	0.[illegible]	0.[illegible]	-0.[illegible]	-0.[illegible]	-0.[illegible]	-0.[illegible]	-0.[illegible]	[illegible]
11	0.[illegible]	-0.[illegible]	-0.[illegible]	0.[illegible]	-0.[illegible]	-0.[illegible]	0.[illegible]	-1.[illegible]	[illegible]
12	0.[illegible]	-0.[illegible]	0.[illegible]	-0.[illegible]	-0.[illegible]	0.[illegible]	-0.[illegible]	-0.[illegible]	[illegible]

O ····O interaction.

(a) The numbers of the atoms are as in Figure 3.7.

(b) A negative value indicates a more stable interaction in the syn intermediate.

	10	11	12
10	0.[illegible]		
11	0.[illegible]	-0.[illegible]	
12	0.[illegible]	0.[illegible]	-0.[illegible]

-0.[illegible] Energy difference for 1-centre terms = sum of diagonal matrix elements.
-0.[illegible] Total energy difference = sum of above matrix.

Table 3.11 Energy Difference Matrix (SYN-ANTI) For S_N2' Intermediates.

E (SYN (H fixed in C-C-C plane) − ANTI)

	1	2	3	4	5	6	7	8	9
1	[illegible]								
2	[illegible]	-0.0002531							
3	0.0171363	0.0012019	[illegible]						
4	0.0071312	0.0012021	[illegible]	[illegible]					
5	-0.0011312	-0.0136235	0.0017059	[illegible]	[illegible]				
6	-0.0011319	-0.0136268	-0.0025772	0.0017078	0.0142779	[illegible]			
7	0.0187553	0.0136584	0.0023271	-0.0004265	0.0004237	[illegible]	-0.0037917		
8	-0.0072181	0.0012941	-0.0004597	0.0003497	-0.0001236	[illegible]	-0.0016752	0.0075301	
9	0.0037553	0.0001263	-0.0045293	0.0023204	0.0001836	0.0008253	0.0006749	-0.0025275	-0.0037918
10	-0.0072477	0.0012959	0.0013497	-0.0005621	-0.0045884	-0.0001223	-0.0005278	-0.0015716	-0.0016745
11	0.0002852	0.0000913	-0.0002872	0.0012541	0.0011947	-0.0004753	-0.0015469	0.0015635	-0.0008293
12	0.0002853	0.0000913	-0.0012541	-0.0002871	-0.0004753	0.0011992	-0.0008293	0.0015861	-0.0015472

	10	11	12
10	0.0075303		
11	0.0015000	-0.0004924	
12	0.0016034	0.0025900	-0.0004915

-0.0142334 Sum of 1-centre energy difference terms.
-0.0016233 Total energy difference.

Table 3.12 Energy Difference Matrix (SYN (H fixed, planar)-ANTI) For S_N2' Species.

stabilises the central carbon atom, in itself not surprising, but at the expense of the two 1-centre oxygen terms.

In line with our analysis of the $CH_5^{\oplus}$ system, we must now study a model reaction starting from a symmetrical 'reactant', which possesses separate σ and π orbitals, and can proceed via pathways maintaining different elements of symmetry, to the two intermediates. However with our present system, two 'reactants' are possible. These are shown in Figure 3.8, together with details of the necessary distortions which must take place to move towards the intermediates. The flat model has the classical σ-π separability, with five 2p atomic orbitals on the main atoms making up the basis set for the π and π^* orbitals. In the rotated form there are seven π/π^* orbitals, since in addition to those mentioned in the planar model, there are two π-symmetric functions made up of antibonding combinations of the 1s atomic orbitals on the two pairs of hydrogens (7-8 and 9-10) that are now symmetrically located above and below the molecular plane.

The flat, rotated, and distorted forms were studied using bond lengths and bond angles derived from the calculations on the intermediates. (These were later repeated, where necessary, with the longer C.....O bond lengths). Without going into the details of the analysis, it was found that using the rotated form and the distortions practised upon it, it was not possible to obtain a clear picture of the processes that were occurring on moving towards the intermediates, in terms of HOMO-LUMO interactions. The reasons for this appear to be as follows. In order to describe the m.o.s of a molecule, parts of which have been rotated (i.e. in the distortions required), in terms of the unrotated m.o.s, one really needs to rotate the basis set on the atomic centres that move, as well as moving the centres and the corresponding orbitals

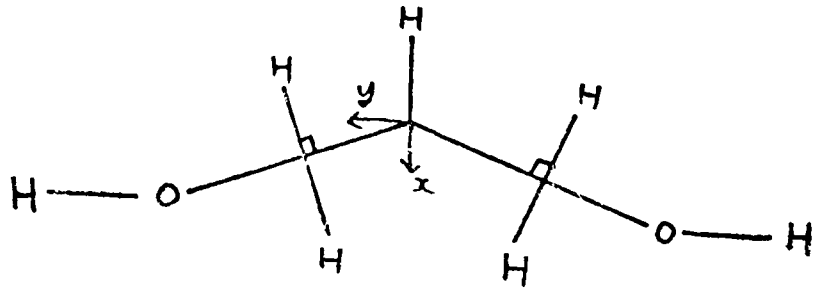
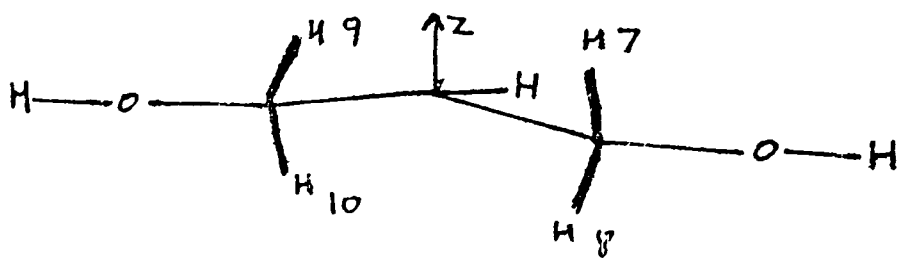
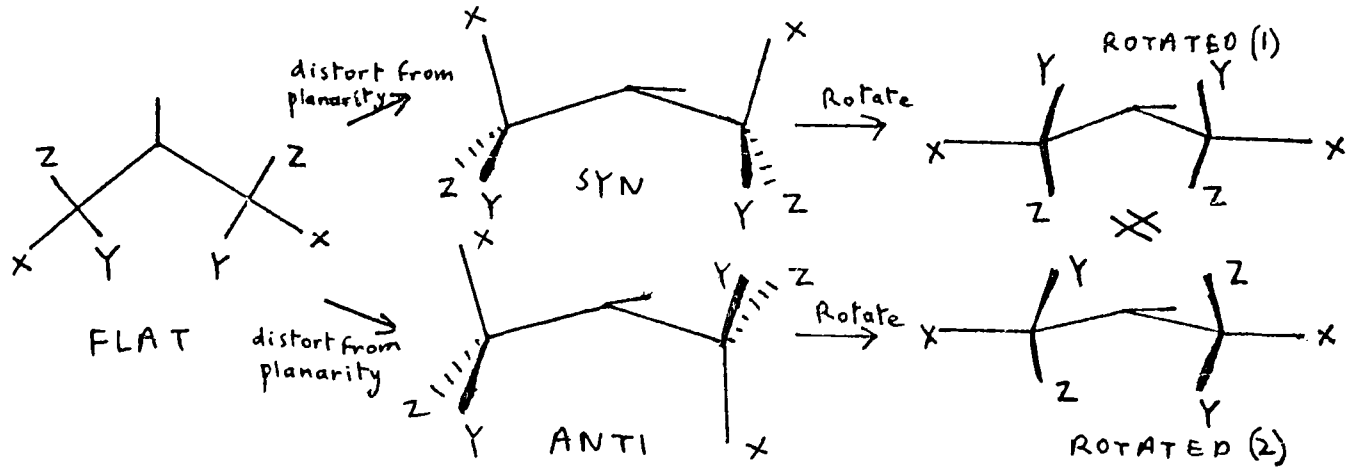
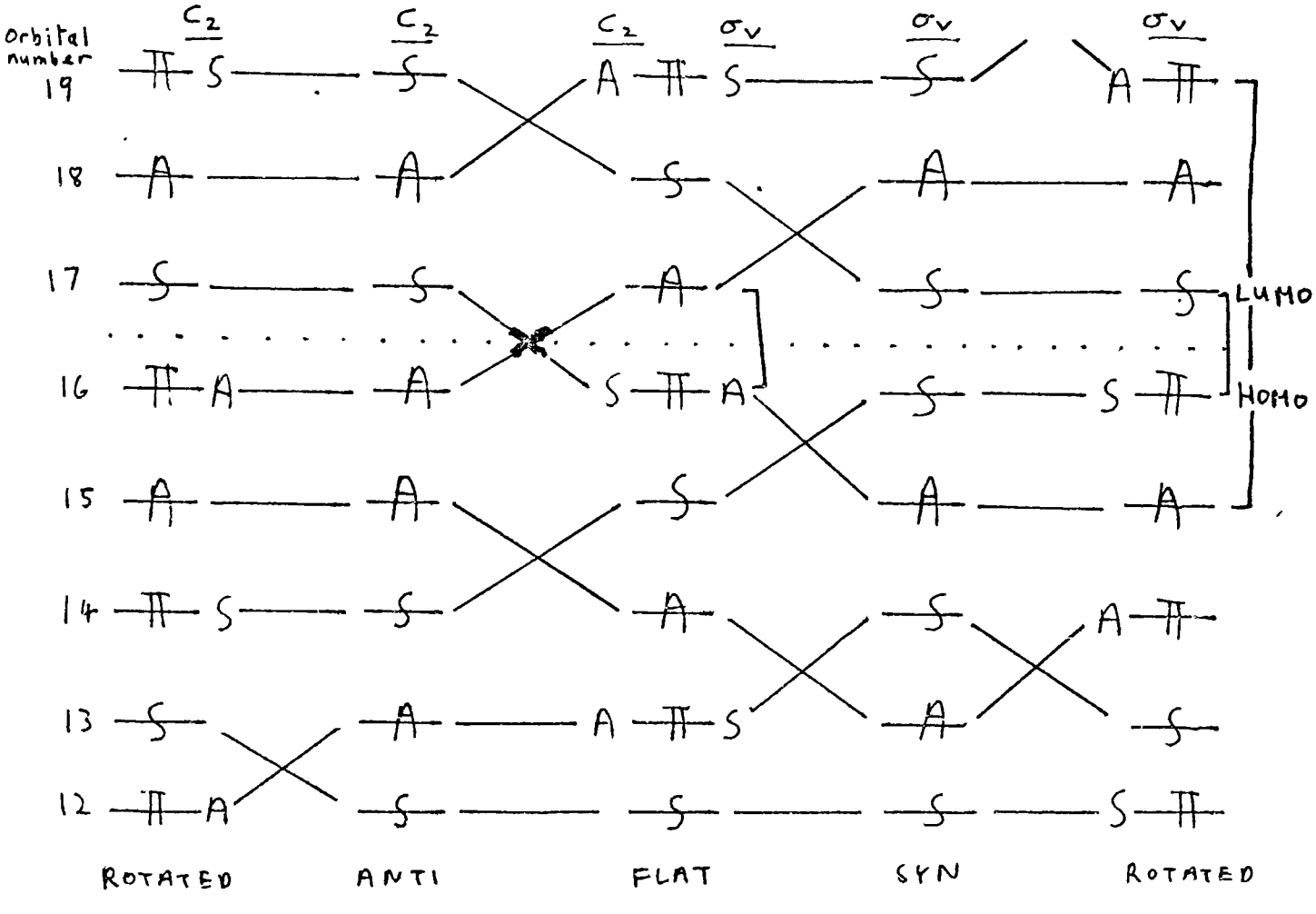
MODELS	DISTORTIONS	FINAL INTERMEDIATES
 FLAT All atoms in same plane.	(a) Raise both OH's by small amounts.	SYN (H Fixed, planar)
	(b) Raise one OH and lower the other by the same amounts.	ANTI
	(c) Raise both OH's and lower the central hydrogen	SYN
 ROTATED All atoms besides hydrogens 7, 8, 9 and 10 are in the same plane.	(a) Rotate both CH_2OH groups in disrotatory manner.	SYN (H fixed, planar)
	(b) Rotate both CH_2OH groups in conrotatory manner.	ANTI
	(c) Rotate both CH_2OH groups in disrotatory manner and lower central hydrogen.	SYN

Figure 3.8 Symmetrical Models and Related Distortions for S_N2' Species.

translationally to the new atomic positions. This is a very complicated process to simulate, since it requires a rotation matrix to be employed for each axis of the molecule about which rotation occurs. Therefore the simple process of multiplying together and summing the coefficients of each atomic orbital in the new and old m.o.s is only appropriate to translational distortions of a 'reactant' and not to rotations. However symmetry considerations relating to the HOMO π orbital and the LUMO σ^* orbital lead to the correct prediction for the preferred intermediate, using both the flat and rotated models and these observations will be noted below.

Another more subtle difference between the two models, which in the particular example of the S_N2' can be turned to our advantage, is as follows. In Figure 3.9 are shown the two ways of going from the flat to the rotated model, via the two intermediates. We have now distinguished between the two hydrogens and it can be seen that these processes lead to different rotated models (conversely the use of one rotated model is related to two reactions (syn and anti) involving different planar reactants, with respect to groups X and Y). Now we know that the syn and anti intermediates are the lowest energy forms of the molecule possessing these two different kinds of symmetry and therefore they must be the intermediates for the reactions being considered, namely the interconversions of the flat and rotated forms. The qualitative energy profile is given in the figure, together with an orbital correlation diagram for the 5 HOMO's and 3 LUMO's of the various species derived from the MINDO calculations (the other OMO's all correlate within the sets). The symmetries of the orbitals are most easily identified by considering the coefficients of the 2s and $2p_z$ (π) orbitals on the central carbon atom. The values of these coefficients (zero or non zero) for the orbitals of interest, are given in Table 3.13.





C_2 symmetry element preserved.

σ_v symmetry element preserved.

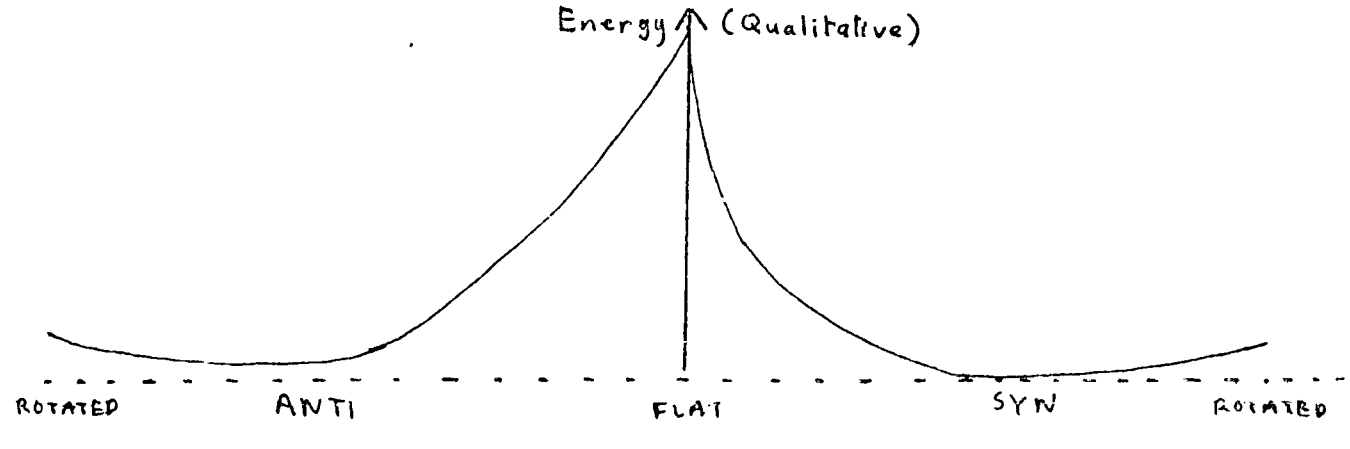


Figure 3.9 Interconversions of Flat and Rotated Models (S_N2').

Orbital Number	Flat		Syn	Anti	Rotated	
	2s(σ)	2p$_z$(π)	2s(& 2p$_z$)	2s	2s(σ)	2p$_z$(π)
12	✓ (σ)	—	✓	✓	— (π)	✓
13	— (π)	✓	×	×	✓ (σ)	—
14	× (σ)	—	✓	✓	— (π)	×
15	✓ (σ)	—	×	×	× (σ)	—
16	— (π)	×	✓	×	— (π)	✓
17	× (σ)	—	✓	✓	✓ (σ)	—
18	✓ (σ)	—	×	×	× (σ)	—
19	— (π)	✓	✓	✓	— (π)	×

where ✓ = non-zero , × = zero

— = inapplicable (i.e. in flat and rotated m.o.5, we have complete σ(2s) − π(2p$_z$) separability.)

Table 3.13 Occupancies of Atomic Orbitals on The Central Carbon Atom in S_N2' Models.

We observe that the 'syn' interconversion is orbital symmetry-allowed and that the 'anti' conversion is orbital symmetry-forbidden and involves a HOMO-LUMO crossing. This is exactly analogous to the Woodward-Hoffmann treatment of pericyclic reactions (see Chapter 1). However in this case we have intermediates and not transition states and therefore the HOMO-LUMO crossing does not occur near the intermediates. It would seem however that it is still valid to infer that the 'forbidden' pathway should proceed via the less stable intermediate, which we actually know to be the case from our calculations on the intermediates. Here therefore is an example in which we need only perform calculations on the flat and rotated models (without distortions) to predict the preferred mode, by an orbital correlation diagram. This, as will be seen, is not always the case and may in fact be the exception rather than the rule.

The implication of a HOMO-LUMO crossing is obviously that the LUMO becomes more stable, relative to the HOMO, as reaction proceeds. This might appear to be a first order perturbation energy change, in that the HOMO and LUMO stabilise or destabilise as the interatomic distances change during reaction. However in terms of our breakdown, the MO's are continuously re-formed at points along the reaction pathway and this is essentially a mixing, i.e. second order process. Thus the description of an electrocyclic reaction, for example, as involving the conversion of a π bond into a σ bond, by rotation of the end a.o.s of the π system, is formally correct, but is misleading. A more appropriate description is to say that the σ and π orbitals mix to form what can be considered as a rotated π orbital and it is this mixing which must be studied. This has the advantage of being applicable even when a HOMO-LUMO crossing is not present, as we shall see is often the case, since this mixing process still occurs and can be analysed.

Returning to the flat species, we noted that five π m.o.s could be formed from the five $2p_z$ functions on the main atoms. Now from the calculation on the flat geometry, we find that four of these m.o.s, which can accommodate eight electrons, are completely filled. (The four m.o.s are, qualitatively, the same form as the first four m.o.s of pentadiene, weighted towards the more electronegative oxygen atoms). However from the density matrix of the syn, syn (H fixed, planar) and anti intermediates, we know that these same $2p_z$ functions finally contain in total 5.73,6.04 and 6.18 electrons respectively. Thus we can confidently say that π orbital depopulation of the planar species is of importance and that this is greatest in the syn intermediate (we may note in passing that the majority of the difference between syn and anti depopulation is associated with movement of the central hydrogen, since the figure for the syn (H fixed, planar) 'π' orbital population is close to that of the anti).

The symmetries of the flat m.o.s (see Figure 3.9) are such that the HOMO π orbital can only transfer electron density to the LUMO σ^*, if the σ_v symmetry element is preserved, which leads to the syn intermediate. Hence our new criterion for prediction, derived from the $CH_5^{\oplus}$ system, (i.e. investigation of the symmetry of HOMO and LUMO orbitals) seems to apply in this example also. This is still true, if one uses the rotated m.o.s as the basis for prediction. It should be added that in this case it might be more correct to consider π - σ^* and σ-π^* interactions as the rotated forms are geometrically and electronically very similar to the intermediates. Thus a <u>mutual</u> electron transfer between π and σ orbitals is more likely to take place, rather than exclusive π to σ^* transfer. The relevant orbitals pairs are ϕ_{16}, ϕ_{17} (π,σ^*) and ϕ_{15}, ϕ_{19} (σ,π^*). Symmetry considerations again predict

that the syn form will be preferred.

In order to check these conclusions, the flat model was distorted in the three ways described in Fig.3.7. In all cases the relevant atoms were moved by 0.1 a.u. above or below the plane. The matrix of c_{ijo}'s and the values for P_{jo} for orbitals 14-19 (i.e. 3 HOMO's and 3 UMO's) are given, for the syn and anti distortions, in Table 3.14. The values for the syn (H fixed) distortion are virtually the same as the syn distortion. The large electron transfer (.040) to the LUMO σ^* in the syn distortion can be seen and this can almost exclusively be attributed to transfer from the HOMO π (0.0395). This HOMO-LUMO interaction in the syn distortion is the only interaction of any magnitude between a <u>filled</u> and unfilled orbital in either distortion. However we may also note the large mutual interaction between the LUMO σ^* (orbital 17) and the LUMO π^* (orbital 19) for the anti distortion. This process, combined with the symmetry forbidden π-σ^* mixing, results in the orbital crossing discussed previously.

We must still prove that the HOMO-LUMO mixing can account for the major part of the energy difference found between the syn and anti distortions. This is shown to be so in Table 3.15. The values for ΔE_{TOTAL} (relative), $\Delta E^{S.C.F}$ (relative) and e''_{ijo} were calculated as described for $CH_5^{\oplus}$. The contribution of the energy of the HOMO-LUMO interaction is just over 75% of the total (relative) change in $E^{S.C.F.}$ The minor σ-π^* interaction is seen to be still of significance in stabilising the syn model. The small remaining contribution may be from other second order stabilisations or in this case might be associated with first order perturbation energy differences. The HOMO-LUMO electron transfer is nevertheless dominant.

It is not productive to describe the final m.o.s of the intermediates in terms of the flat m.o.s, because of the gross electron density changes

(a) Distortion Towards ANTI

C_{ijo}

j_o → / i →	14	15	16	17	18	19
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						

P_{jo}						
	(HOMO-1)σ	HOMO σ	HOMO π	LUMO σ*	(LUMO+1)σ*	LUMO π*
j_o →	14	15	16	17	18	19

(b) Distortion Towards SYN

C_{ijo}

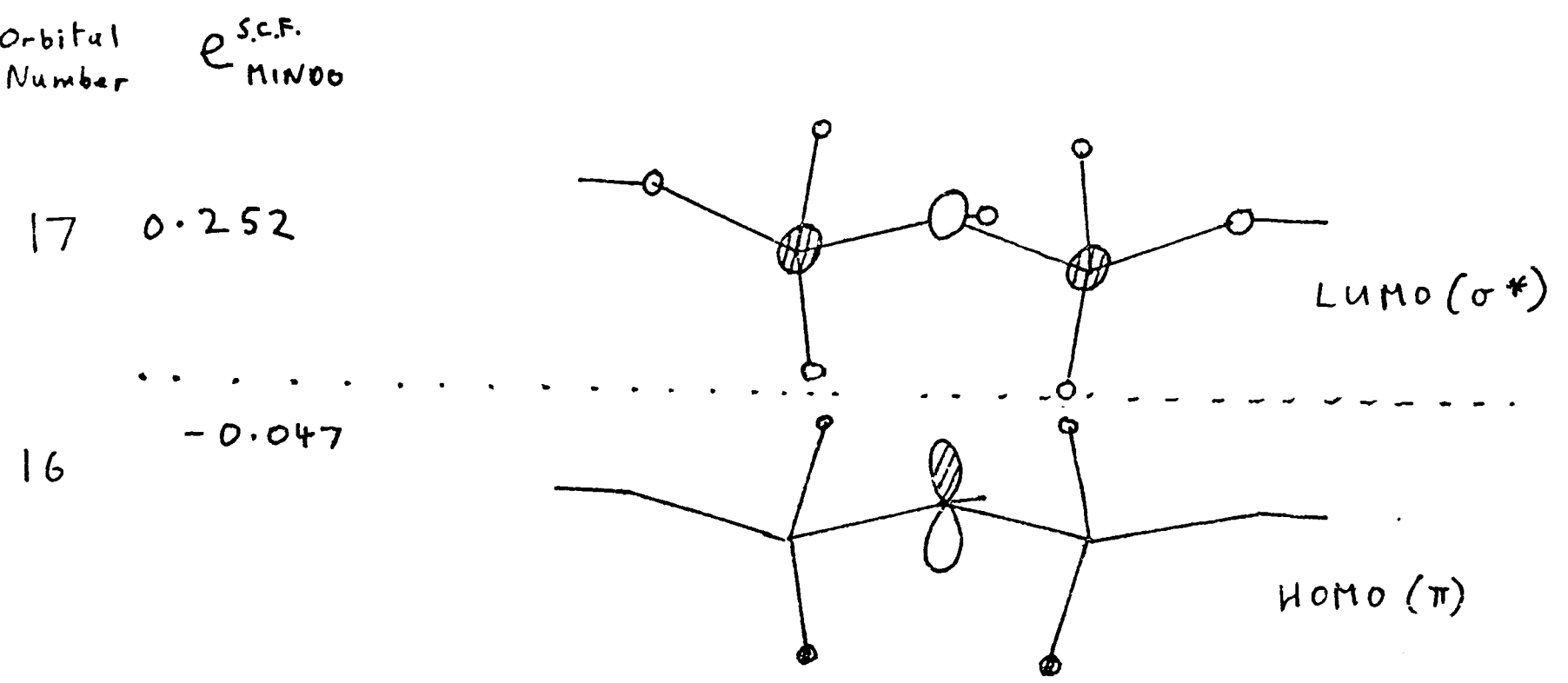
j_o ↓ / i →	14	15	16	17	18	19
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						

P_{jo}						
	0.99999913	0.99711695	0.99963395			
	(HOMO-1)σ	HOMO σ	HOMO π	LUMO σ*	(LUMO+1)σ*	LUMO π*
j_o	14	15	16	17	18	19

Table 3.14 S_N2'; Matrix of Values For C_{ijo} and P_{jo} For SYN(H free) and ANTI Distortions.

	SYN	ANTI
ΔE_{TOTAL} (relative)	0	0·00123
$\Delta E^{S.C.F.}$ (relative)	0	0·01358
$e''_{HOMO-LUMO}$ ($\pi-\sigma^*$)	−0·01030	0
($e''_{HOMO\,\sigma-LUMO\,\pi^*}$)	−0·00104	0

Table 3.15 Energetics of The SYN and ANTI Distortions to The Flat S_N2' Model.



	SYN	ANTI	[SYN (Hplanar)]
P_{LUMO}	0·086	0·017	[0·047]
$\therefore e''_{LUMO}$ (approx.)	−0·035	−0·007	
			$\therefore \Delta e''_{LUMO} \doteq 0·028$
ΔE_{TOTAL} (relative)	0	0·00358	
$\Delta E^{S.C.F.}$ (relative)	0	0·0166	

Figure 3.10 HOMO and LUMO of The Rotated S_N2' Model and The Contribution of The LUMO to the MOs and Energies of The Intermediates.

that are involved in the interconversions of these species. However this is not true if we start with the rotated model. It will also be possible to decide whether HOMO-LUMO interactions in the rotated model are important and whether they confirm the origin of stabilisation, i.e. 1-centre terms. The HOMO and LUMO of the rotated model are given in Figure 3.10. Electron transfer to the LUMO will obviously increase the s character of the main atoms and thus the 1-centre stabilisation. Note that stabilisation at all five main atom centres (and the central hydrogen) was found for the (syn (H fixed, planar) - anti) energy difference matrix (Table 3.12). The movement of the central hydrogen out of the plane, not unexpectedly, leads to other interactions also (giving the final energy difference matrix, Table 3.11).

The transfer of electron density from HOMO to LUMO, combined with the associated rotations, most strongly affects the non-bonded atom interactions between hydrogens 7,8,9 and 10. This was very apparent when initial studies were performed using density matrix (Epiotis) and overlap population indices. Besides the fact that this did not coincide with our original HMO interpretation of syn stability, in terms of main atom effects, the overall sum of both these indices favoured the anti geometry (especially the density matrix index)! It was these results in particular that led to the search for a more fundamental and accurate index, resulting in the total energy, and orbital energy, partitioning methods.

Since the LUMO is essentially a combination of s orbitals, with no significant 2p contributions, rotation to the intermediates and the 'translational' breakdowns of the intermediates' m.o.s in terms of the rotated m.o.s may still apply to it alone. This is so, since rotation of an s orbital basis function leaves the basis function unchanged

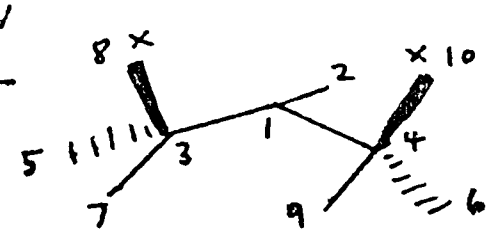
and hence the previously described problem of orbital breakdown in the rotation context disappears. Thus the calculated sum of the LUMO contributions to the final m.o.s of the intermediates are still informative. These are given, in terms of summed electron densities, in Figure 3.10. (The fact that they are small is a confirmation that the breakdown can be applied usefully to these contributions). Approximate values for the energy changes associated with these contributions are given in order to show that these interactions alone are sufficient to explain the total energy differences, E_{TOTAL} and $E^{S.C.F.}$ (The second order energies are approximate, since the energy gap varies for the LUMO contributions to the different OMO's and an average figure was used. Also the large overall changes mean that the perturbation theory framework does not rigorously apply to these distortions).

We can see that the HOMO-LUMO interaction is both a necessary and sufficient factor to account for syn stabilisation. This also implies that σ-π^* stabilisation in this system is not necessarily as important as we have previously suggested. We have therefore found that whether we take the flat or rotated forms as our models, our thesis concerning the decisive importance of HOMO-LUMO interactions still holds.

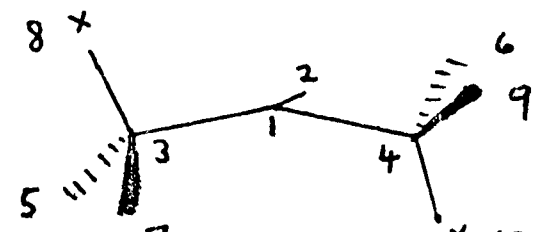
b) S_E2'

As a first stage in studying the S_E2' reaction, we used as models the above intermediates minus two electrons. This also showed the effect of depopulating the all important HOMO. The two intermediates were then allowed to toally optimise their geometries. The only major change that ensued was that the central hydrogen in the syn intermediate returned to the c-c-c plane, now that the central carbon did not carry a negative charge. The energies of these various species are given in Table 3.16.

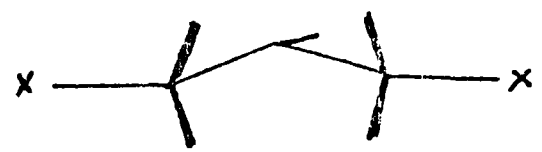
S_E2'



SYN (σ_v)



ANTI (C_2)



ECLIPSED CATION (C_{2V})

OPTMO

		SYN	ANTI
(a) $OH^{\oplus}$ as electrophile + allyl alcohol.	(i) Same geometry as S_N2'.	6·1	0
	(ii) Optimised geometry.	17·7	0

		SYN	ANTI	ECLIPSED CATION	PROPENE ($+H^{\oplus}$)
(b) $H^{\oplus}$ as electrophile + propene.	(i) H's in place of OH's, geometry as in (a)(ii).	14·1	0		
	(ii) Optimised geometry.	0·35 (C_{2v})	0	4·1	188·7
	(iii) GAUSSIAN 70 results. (POPLE)	0	?	—	~190·0
	(iv) Experimental (FRANKLIN).	0			179·2 ± 2·1

Table 3.16 Relative Energies (Kcal/mole) of Species Involved in S_E2' Model Reactions.

However the system with OH groups represents the attack of $OH^{\oplus}$ on allyl alcohol. A more chemically realistic reaction, which was the only one studied in detail, was the S_E2' attack of a proton on propene Initially the incoming and departing hydrogens were placed in the positions of the oxygen atoms found in the optimised geometries above, but then total optimisation was performed on the syn and anti species (for the optimised geometries, see Appendex 2 - numbers 9 and 10). The C...H optimised distances were virtually the same as the other C-H bond lengths. However this is not surprising as these 2-propyl cation intermediates are the most stable forms of any $C_3H_7^{\oplus}$ species, as shown by exhaustive calculations performed by Pople et. al. (1972a) on nine $C_3H_7^{\oplus}$ configurations. It is interesting to note Pople's assertion that the most stable species is what we have called the syn intermediate. This appears to contradict the OPTMO results which suggest a small (.35 kcal.) stabilisation of anti versus syn, in line with experiment., until one notices that he restricted the symmetry of his molecule to C_{2v} because of the large number of geometrical parameters, ruling out any possibility of the anti intermediate. Here is another example of assumptions prejudicing conclusions, although to be fair to Pople, he was more interested in the relative energies of different isomers of $C_3H_7^{\oplus}$, rather than in different conformations of one isomer.

In order to derive the relative energies of these cations with respect to propene (and hence the proton affinity of propene also), total optimisation of propene was undertaken. The resulting geometry is given in Appendix 2 (number 11) and the energy is given in Table 3.16, as are the relative energies derived by Pople (1972, 1971a) using GAUSSIAN 70. The Pople energies are those obtained by calculation at the STO 4-31G level using the optimised geometry obtained at the STO-3G level. The experimental relative energies derived by Franklin (1972)

and Chong are also given. For completeness, full OPTMO optimisation was also performed on the other possible C_{2v} conformation (ECLIPSED CATION - see Table 3.16), i.e. with the hydrogens, in the c-c-c plane, pointing away from each other. The final geometry is shown in Appendix 2 (number 12) and the relative energy is in the table.

It can be seen that in this example, OPTMO gives an accurate value for the proton affinity, slightly better than the ab initio results, as Dewar (1972) had previously found with another version of MINDO/2. In other words, the energetics of the formation of this cation are well represented by MINDO/2. This was also the case (in relation to the ab initio studies), for the S_N2' model. However, as will be seen, this is not always so.

Although there is only a small energy difference between the energies of the syn and anti geometries and therefore it may not necessarily be accurately given by theoretical calculations, it will still be the result of a balancing of much larger changes in the molecule. This can be seen from the total energy difference matrix (syn-anti) given in Table 3.17. The numbering of the atoms is as shown above Table 3.16. Many of the matrix elements are an order of magnitude or more greater than the matrix sum. This is also true of the sum of the 1-centre energy difference terms, which once more are the origin of the stabilisation of the preferred species. This sum in turn can almost exclusively be represented by the change in the 1-centre term for the central carbon atom. This energy term (- 0054a.u) can itself be related to the small increase in 2s electron density at the carbon, in the anti intermediate. This small increase (.003) when multiplied by the 1-centre core electron integral, $U_{C_{2s}C_{2s}}$, used in MINDO/2 (-1.825a.u.) gives a value for 2s stabilisation (-0.0061) slightly greater than the overall 1-centre stabilisation term. The large changes in the hydrogen terms (caused by

E(SYN-ANTI)

	1	2	3	4	5	6	7	8	9
1	[illegible]								
2	-0.[illegible]	-0.0010878							
3	-0.[illegible]	-0.0001565	-0.0013285						
4	-0.0034715	-0.0001500	0.0005359	-0.0013269					
5	-0.0124933	-0.0003817	0.0029562	0.0004149	0.0005816				
6	-0.0124933	-0.0003817	0.0004149	0.0029562	0.0015432	0.0005816			
7	0.0035115	-0.0001557	-0.0025958	0.0001564	-0.0029942	0.0003225	-0.0001524		
8	0.0218941	0.0013033	-0.0024052	-0.0019259	-0.0017681	-0.0016545	0.0005360	-0.0018142	
9	0.0035115	-0.0001557	0.0001564	-0.0025958	0.0003228	-0.0012942	-0.0001534	[illegible]	-0.0001524
10	0.0218941	0.0013033	-0.0019259	-0.0024534	-0.0011545	-0.0017681	-0.0001176	0.0018534	0.0005360

	10
10	-0.0018141

0.0066747 Sum of 1-centre energy differences.
0.0005495 Total energy difference.

(a) The numbering of the atoms is as shown in Table 3.16

(b) These intermediates are those that may participate in the reaction of $H^{\oplus}$ with propene.

Table 3.17 Energy Difference Matrix (SYN-ANTI) For S_E2' Intermediates.

the different angles of rotation in the two intermediates) effectively cancel out.

It will be remembered that the simple Hückel theory suggested that destabilisation in the syn geometry is caused by 1, 5 antibonding. In our example this implies that the H_8-H_{10} (the incoming and leaving hydrogens) difference matrix element is the major term. Although this term is seen to favour the preferred anti intermediate, there are many other larger matrix elements between non-bonded atoms and more importantly, the 2-centre difference terms are destabilising for the anti species overall. Therefore the simple Hückel theory gives the correct prediction, but for the wrong reasons.

For our 'model reaction' we can have a rotated or a flat 'reactant', analogous to those of the S_N2' system. However unlike that system, the calculations show that neither of the two interconversions of the S_E2' models involves a HOMO-LUMO crossing (see Figure 3.11). The flat model now has 3 π/π^* orbitals, of which two are filled. Thus the three 2p carbon a.o.s making up the π framework contain four electrons in all. Now we know from the calculations on the syn and anti intermediates that these three a.o.s finally contain 2.48 and 2.41 electrons respectively. Therefore 'π' orbital depopulation is again very strong and notice it is once more greater in the more stable intermediate.

The correlation diagram gives the symmetries of the relevant orbitals. Again one observes that HOMO-LUMO mixing in both the flat (π-σ^*) and rotated (σ-π^*) m.o.s can only occur for the anti distortion. Also π-σ^* mixing in the rotated model (orbitals 7 and 11), which may be important for reasons mentioned previously, is only allowed for the anti distortion.

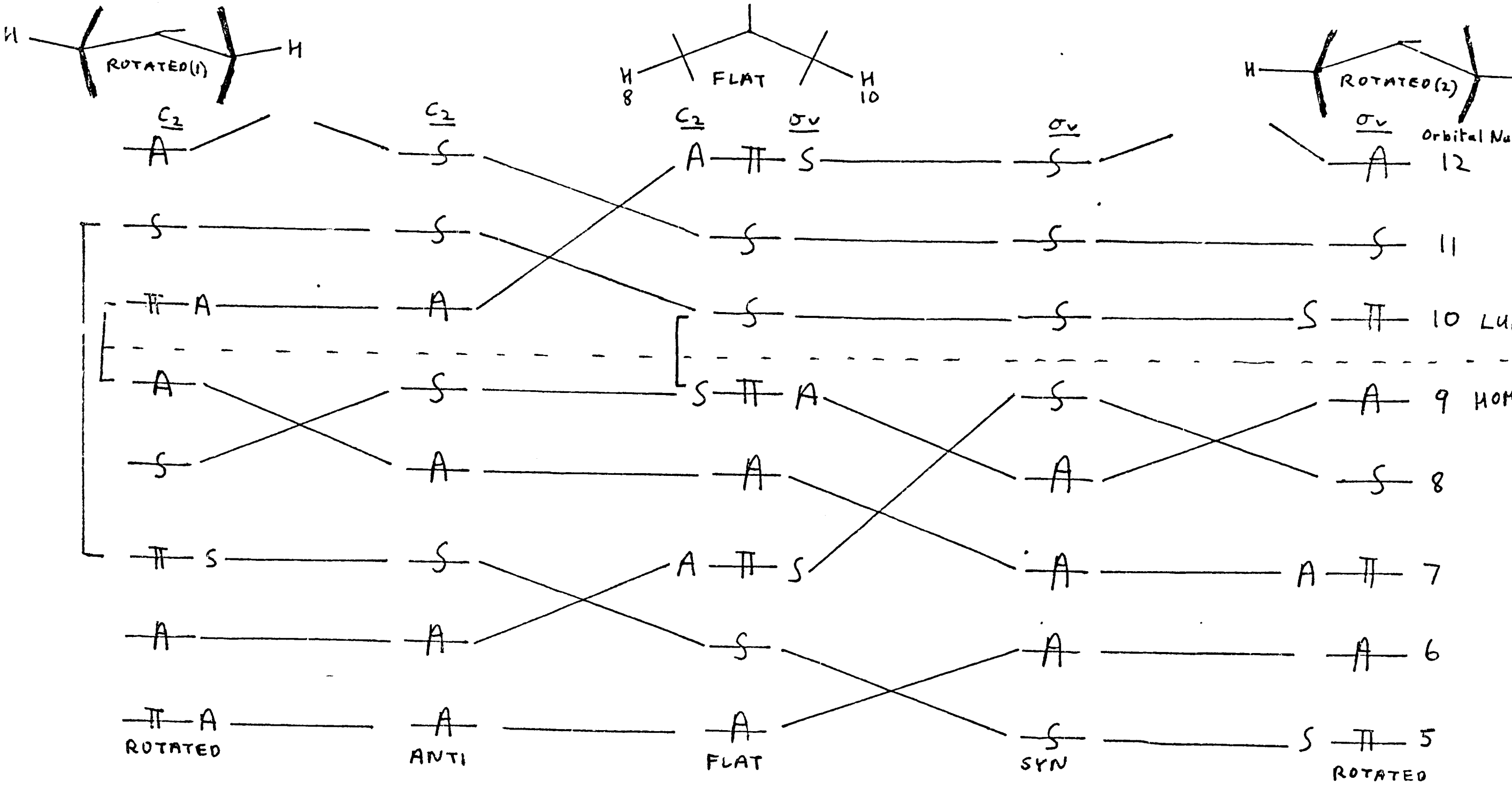


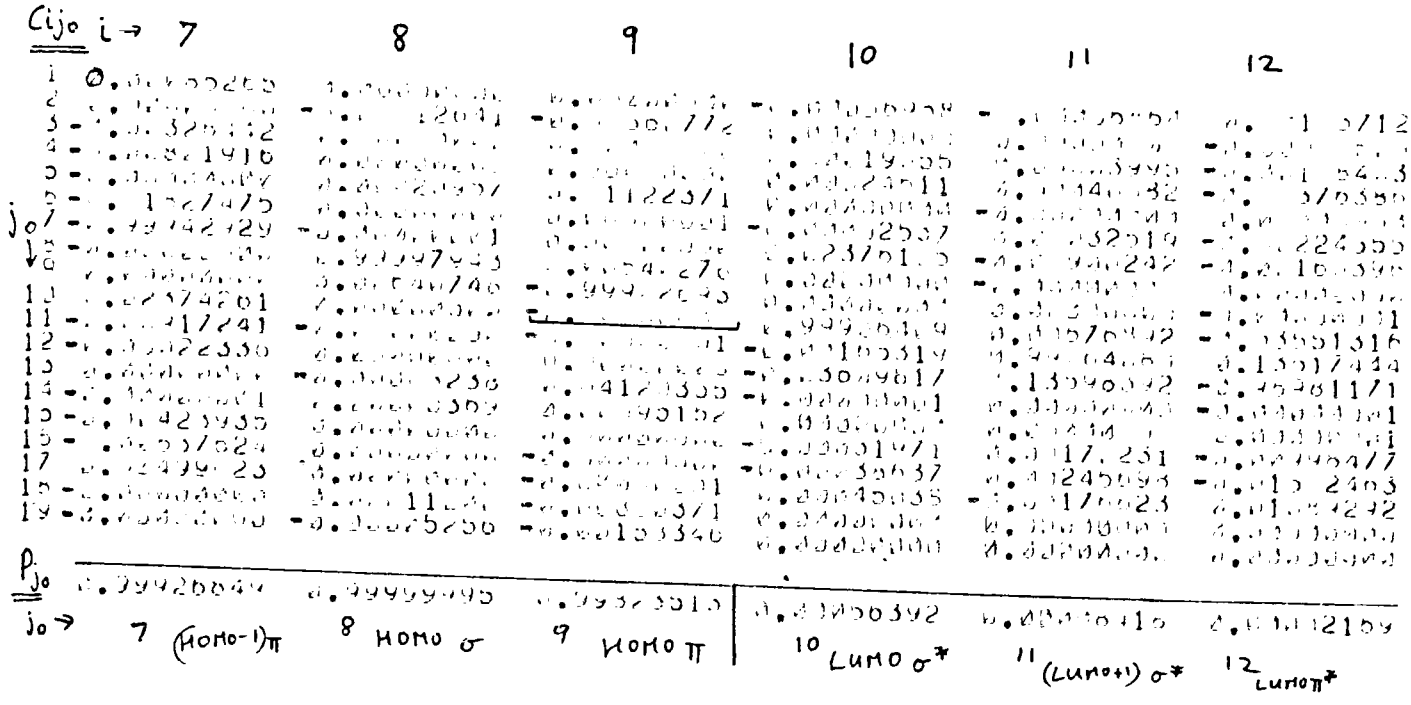
Figure 3.11 MINDO Orbital Correlation Diagram For Interconversions of Flat and Rotated Models ($S_E 2^1$).

The flat model was distorted by moving the hydrogens 8 and 10, 0.1 a.u. above (and below) the plane as before. Of course now there is no difference between syn distortion and syn (H fixed, planar) distortion, since in the syn intermediate the central hydrogen remains in the c-c-c plane. The breakdowns of the new distorted m.o.s and the total electron densities in the old m.o.s (P_{jo}) are given in Table 3.18. The surprising observation is not that the HOMO-LUMO mixing is only present in the anti distortion, but that it is so large. Over .6 of an electron (>·3 from each HOMO electron in the HOMO orbital) is transferred to the LUMO during this small distortion, vastly greater than any other transfer. It need hardly be added that the energy change associated with this electron transfer will dwarf any first order or other second order perturbation energies.

However to investigate the mixing which leads to the m.o.s of the intermediates we will examine the m.o.s of the rotated model, for the reasons given before. The important ones are given in Figure 3.12. It can be seen that HOMO σ - LUMO π^* mixing will not lead to extra s character on the central carbon atom. However the HOMO π - LUMO σ^* mixing will lead to this very result. But one might ask why in this system it appears to be the less favourable (in terms of energy gap) HOMO-LUMO, ϕ_{11}/ϕ_7, interaction that is decisive? The answer must be that the effect of the allowed HOMO σ - LUMO π^* transfer in the anti distortion (ϕ_9/ϕ_{10} mixing) is largely cancelled out by the allowed (HOMO-1)σ - LUMO π^* transfer (ϕ_8/ϕ_{10} mixing) in the syn. As can be seen the two σ orbitals have almost identical eigenvalues and are of very similar form. Thus although their mixings are large, they nullify one another.

If it is generally true for rotated models, that when the HOMO is

(a) Distortion Towards SYN.



(b) Distortion Towards ANTI.

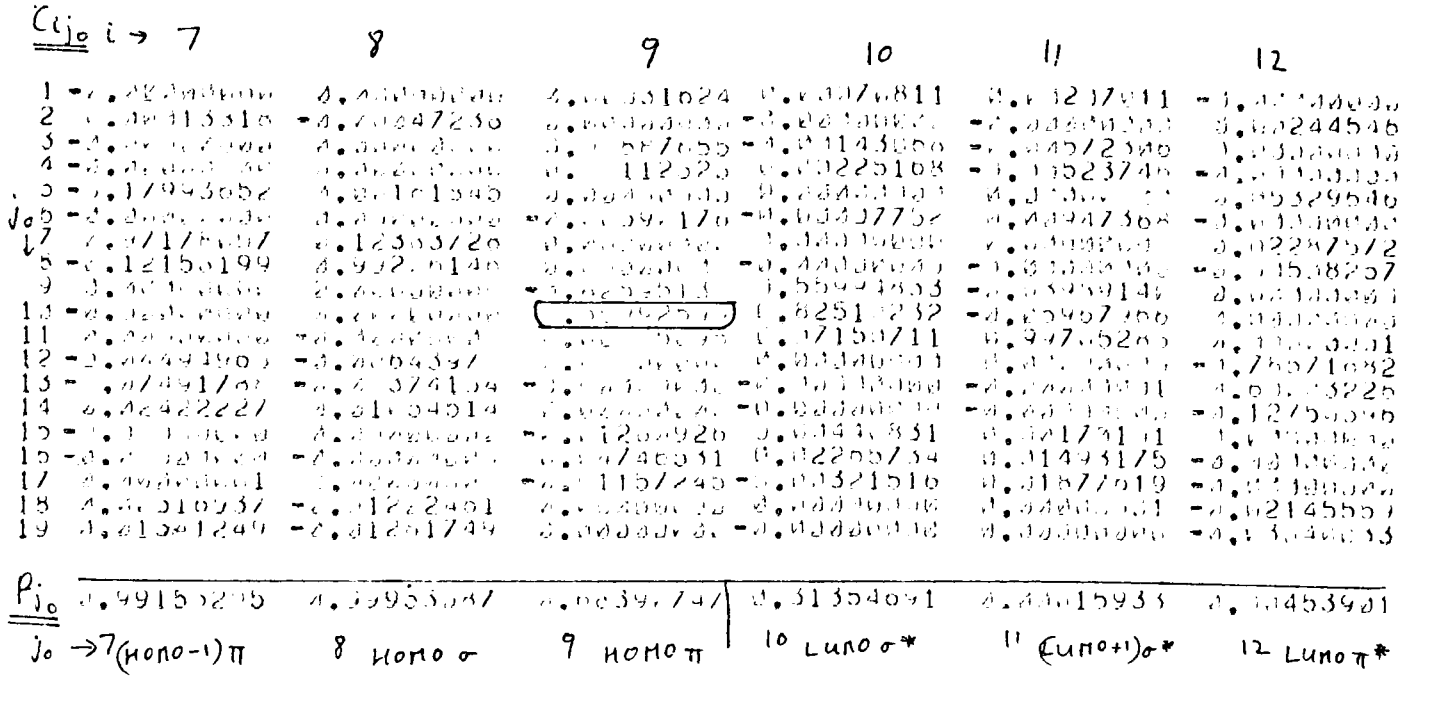


Table 3.18 S_E2'; Matrix of Values For C_{ijo} and P_{jo} For SYN and ANTI Distortions.

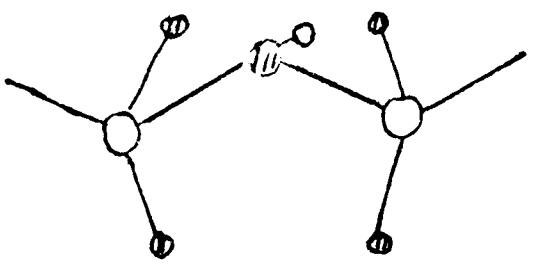
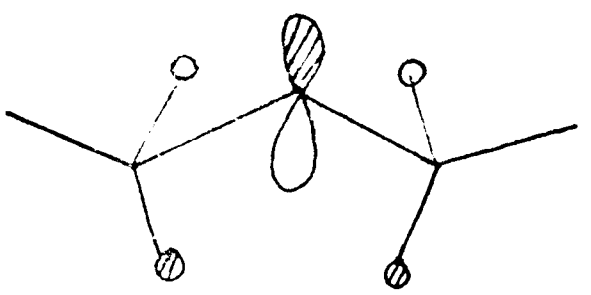
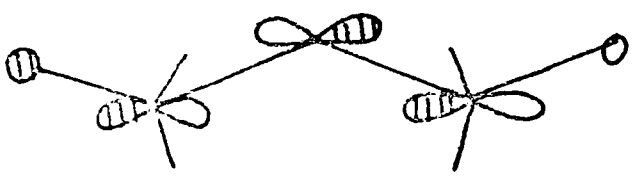
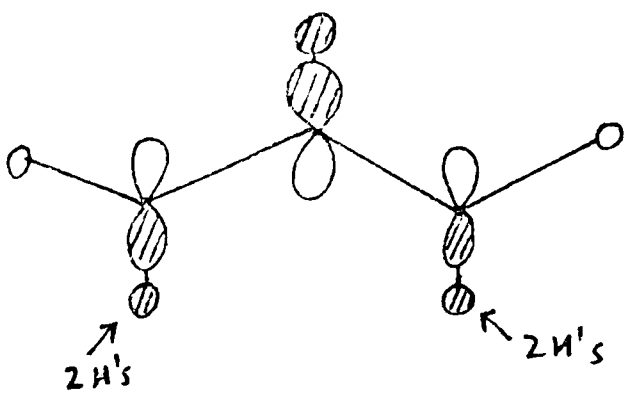
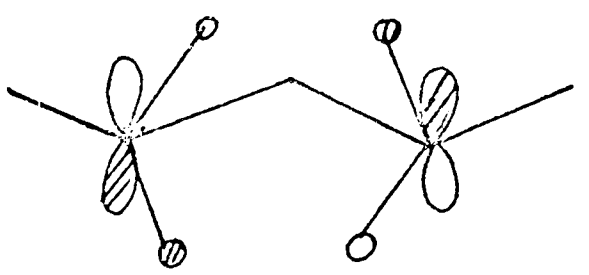
Orbital Number		Type	$\epsilon^{S.C.F.}_{MINDO}$
11		LUMO σ^*	−0·197
10		LUMO π^*	−0·275
		ANTI	
		SYN	
9		HOMO σ	−0·634
8		(HOMO−1) σ	−0·643
7		HOMO π	−0·669

Figure 3.12 HOMOs and LUMOs of The Rotated S_E2' Model.

a σ orbital, there will be another σ orbital of the opposite symmetry and similar form just below it, then we may say that the decisive mixing will always be between HOMO π and LUMO σ*. (It is also possible that MINDO/2 yields rather too high-lying σ orbitals, if photoelectron spectroscopy results are a guideline. This is the conclusion of Heilbronner and Schmeltzer (1975), in relation to their quantitative studies on 'through space' and 'through bond' interactions. If this is so, then the importance of HOMO σ- LUMO π* interactions will be even further diminished). Thus we have again shown, by using either the flat or rotated models, that HOMO π- LUMO σ* mixing is a necessary and sufficient condition for stabilisation of the preferred intermediate. We will now study a system which does not maintain an element of symmetry during reaction.

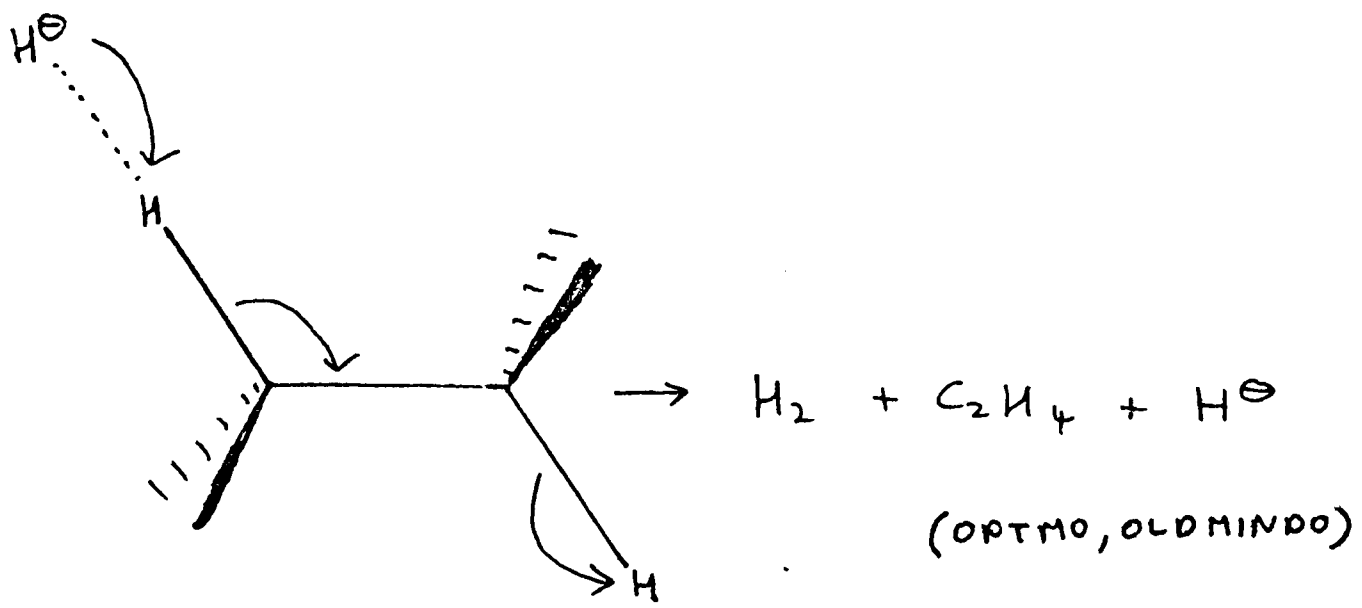
6. The E2 and Associated Elimination Reactions.

In terms of the simple HMO theory, the E2 is an example of a 5-atom, 6-electron system for which the 1,4 bond order factor is destabilising and hence trans elimination, where this interaction is not present, is preferred. The attack of hydride/hydroxide on ethane and ethanol were the models chosen for the E2 reaction (see Figure 3.13). Points were calculated for reactions occurring by cis and trans elimination, using the hydroxide/hydride to hydrogen distance as the reaction coordinate. For the OLDMINDO calculations, the geometries used were the standard experimental values given by Sutton (1959), with the MINDO/2 –required increases in bond lengths (+ 0.1Å for C-H, + 0.15Å for O-H), and the direction of approach was along the C-H bond being attacked.

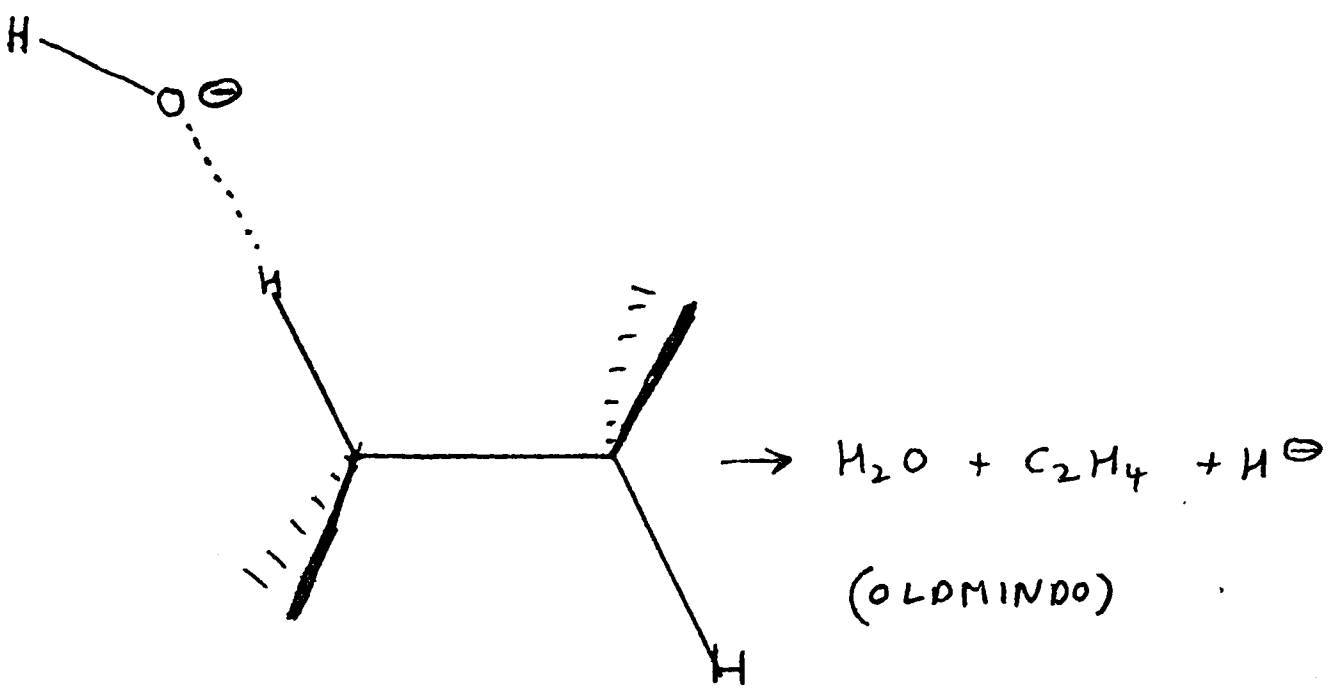
Initially, OLDMINDO studies were performed on the model reactions shown and the base was simply allowed to approach, without any other geometry variation, which is analogous to Fukui's(1968,1971a) C.I. procedure. The energy profiles for these processes are given in Figure 3.14. Two important points may be noted. Firstly, although the energy difference between cis and trans conformations does increase slightly as a base approaches, the major part of this difference (~75%) may be attributed to the normal barrier to rotation in ethane and not to any significant increase in 1,4 antibonding as reaction proceeds. Also one observes that the total energy decreases quite strongly, which suggests the formation of a stable species (in the gas phase).

In order to investigate this latter point more fully, OPTMO calculations were carried out on the systems hydride plus ethane and hydride plus ethanol. The previous method was used but total optimisation was allowed at all points. It was found that the hydride removed a proton

(a.)



(b.)



(c)

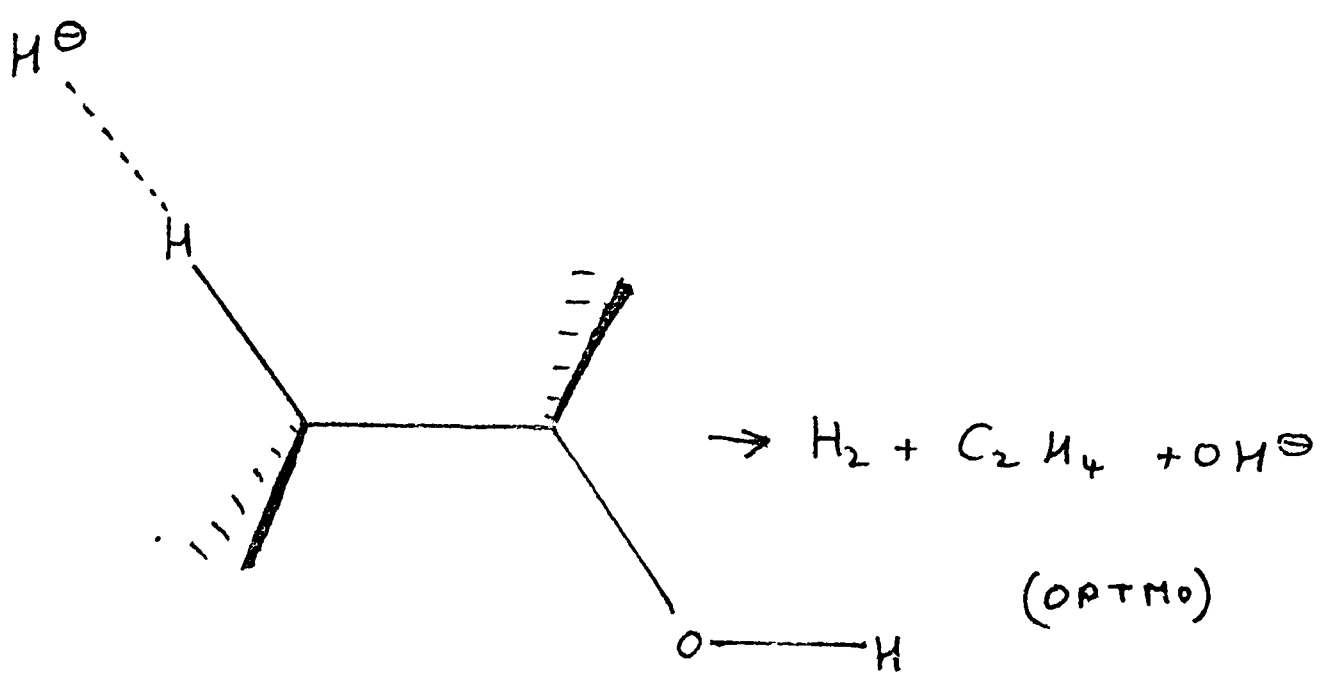


Figure 3.13 Model E2 Reactions

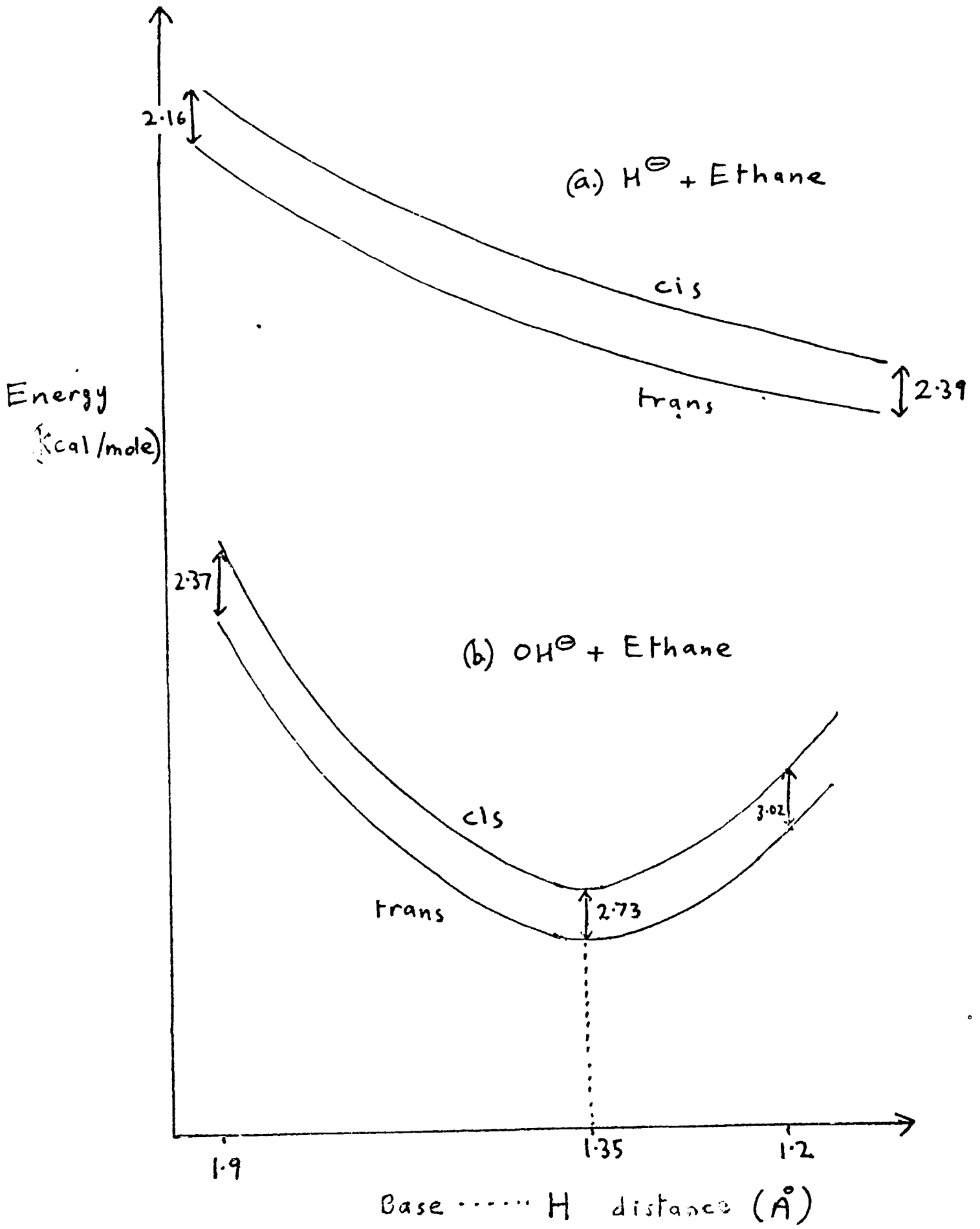


Figure 3.14 Energy Profiles For Attack of $H^{\ominus}/OH^{\ominus}$ on Ethane, Without Geometry Optimisation.

to form a hydrogen molecule, but the resulting species would not dissociate to ethylene plus anion. The species $C_2 H_5^{\ominus}$ was allowed to optimise its geometry and its energy was compared with that of ethane (as a standard). Both Wolfe (1972) and Streitwieser (1970) have carried out ab initio calculations on ethane and ethyl anion using the same basis set for both molecules, with optimisation, and hence their results can be used for comparison. The relative energies, in Kilocalories per mole, are as follows,

	OPTMO	Streitwieser	Wolfe (better total energies)
Ethane	401	502	453
Ethyl anion	0	0	0

The OPTMO stabilisation energy of ethyl anion is therefore too great by at least 50 kilcalories, relative to ethane, assuming the validity of the ab initio calculations. Since the energy difference between the anion and the 'correct' products, hydride plus ethylene (optimised) is found by OPTMO to be 38 kilocalories in favour of the anion, it can be seen that it is this overstabilisation which leads to the incorrectly predicted products. A similar reasoning applies in the case of the relative stability of $(H_2)+ C_2 H_4 OH^{\ominus}$ against $(H_2)+ OH^{\ominus} + C_2H_4$.

However although the wrong products are formed, the observation concerning the relative energy difference between cis and trans modes of reaction still holds. In fact since the anion ($H^{\ominus}$ or $OH^{\ominus}$) does not leave as the OPTMO 'reaction' proceeds, one might expect that any extra (relative to the reactant) 1,4 antibonding in the cis mode of reaction would be increased with respect to the 'correct' reaction. But as we have noted, even in this incorrect OPTMO reaction the

difference btween cis and trans modes is largely explained by the conformational barrier in ethane. We can therefore deduce that in the correct reaction this will still hold, if not more so, i.e. the energy difference between the transition states may be even closer to the value for the conformational barrier in ethane. In other words, in this case conformational/steric interactions are dominant and 'delocalisation' effects play only a small part, if any at all.

It follows from the preceding discussion that the base is present merely in order to facilitate reaction (i.e. to lower the energy barriers to <u>both</u> cis and trans elimination) by removal of a proton and has little effect on the relative energies of cis and trans reactions. Of course, this only applies to the bases that were involved ($H^{\ominus}$ and $OH^{\ominus}$) and might not hold for other bases. This being so, we can initially look at the reactant without base, in terms of our previous analyses. We shall first study ethane itself, since in its staggered and eclipsed conformations it preserves different symmetry elements of interest (C_2 and σv, respectively) and then look at ethanol. Finally these two molecules will also be investigated when a base is present.

(a) <u>Ethane</u>.

Because we could not simulate the E2 reaction of ethane plus base, we have no idea of the bond lengths and bond angles in the transition states. However in this and subsequent sections, we will be interested in merely determining whether the previous conclusions concerning HOMO-LUMO interactions still hold and whether they lead to the correct predictions for conformational preference. This will be decided by more qualitative and less exhaustive analysis than was previously employed, since this was only necessary in order to

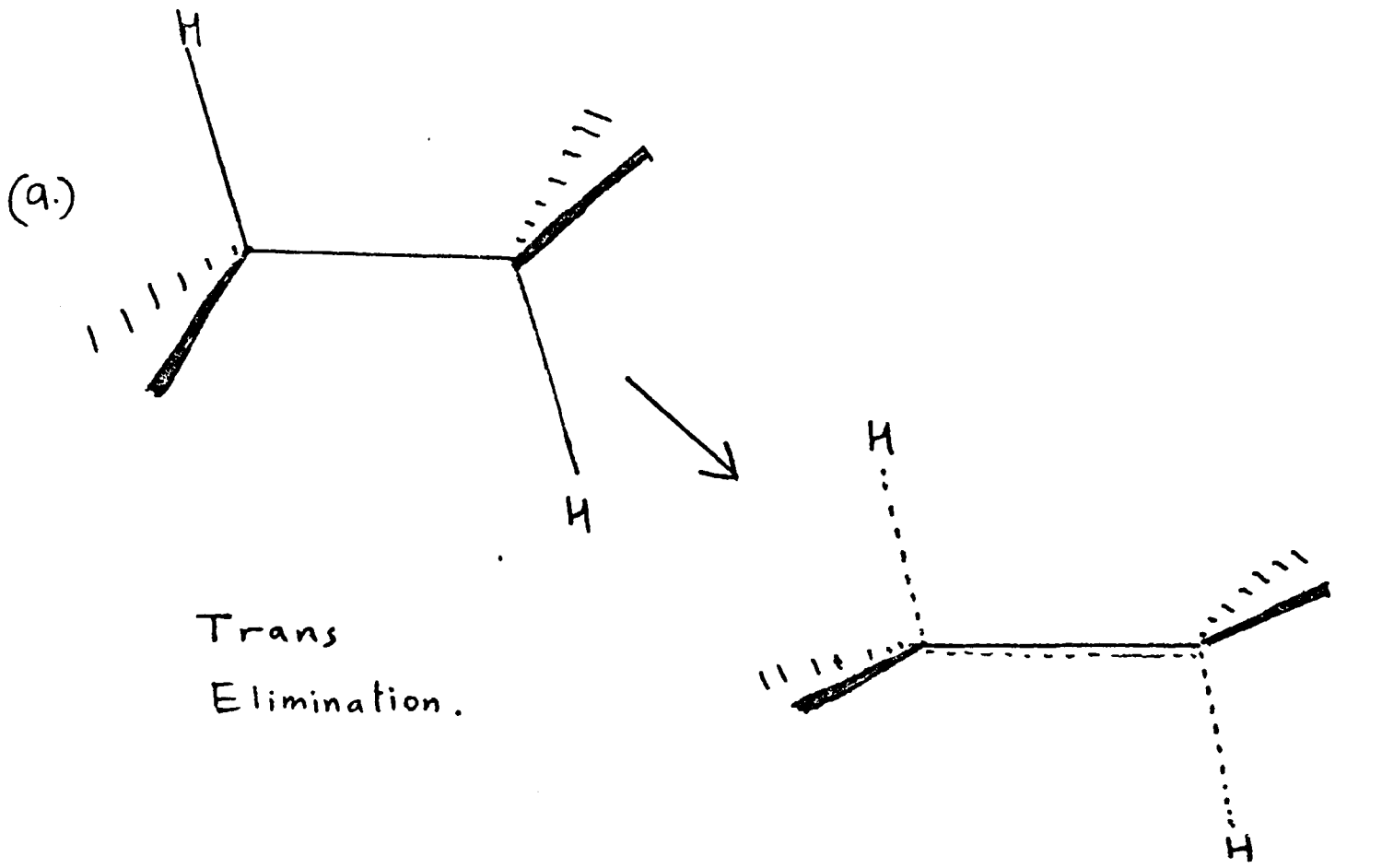
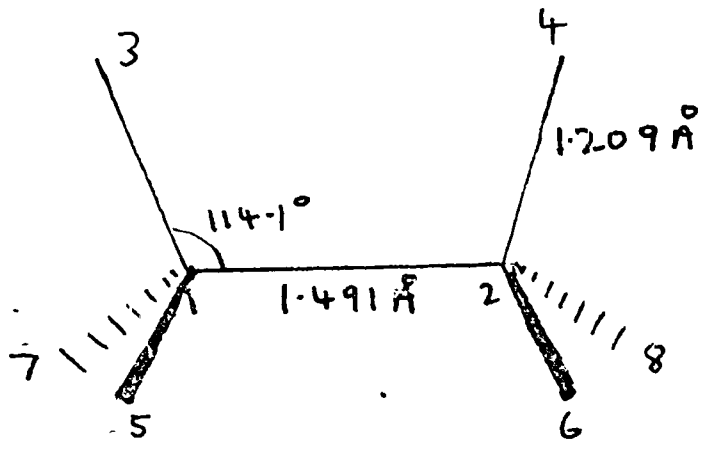


Figure 3.15 Elimination Reactions For Which the Eclipsed and Staggered Forms of Ethane Can Be Considered as Models.

develop and confirm the thesis concerning HOMO-LUMO interactions.

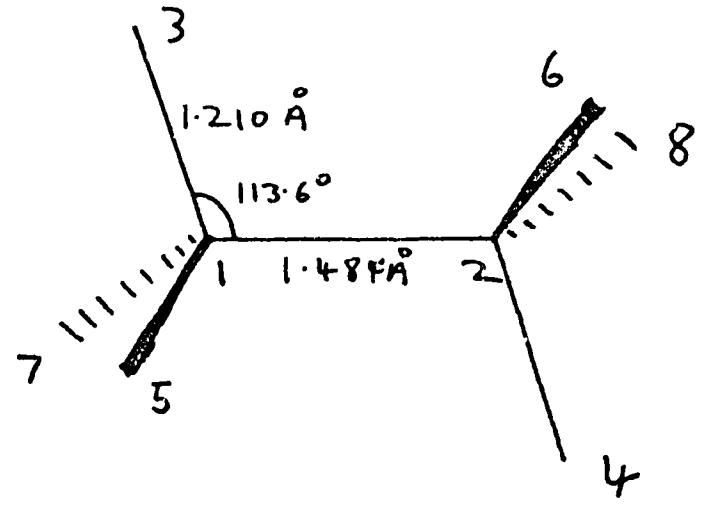
Thus, in the first instance, the eclipsed and staggered forms of ethane will be used as models for the decisive parts of the two transition states possible in the E2 reactions. In other words, the base seeming to be irrelevant, we shall think of the E2 reaction (based on the ethane model) in the terms shown in Figure 3.15. The geometries of the two extreme conformations of ethane were totally optimised and the details of the final geometries are given in Figure 3.16. The energy difference matrix was calculated and is also given in the Figure (the atom numbering is the same as in the diagrams). It can be seen that it is the 2-centre energy difference terms that destabilise the eclipsed form, the greatest being the $H_3....H_4$ term (i.e. 1,4 antibonding) and the C-C term. The possible implications of this behaviour, which is different from the previous 1-centre stabilisations, will be discussed below.

Calculations were performed on the flat model shown in Figure 3.17, and on distorted cis and trans forms, in which hydrogens 3 and 4 were moved by 0.1 a.u. above (and below) the molecular plane. The m.o. breakdown matrix (Cij_o's) and the values of P_{j_o} are also given in the Figure. We can again see that both HOMOσ-LUMOπ^* and HOMOπ-LUMOσ^* interactions are only possible in the 'trans' distortion which leads to the preferred model 'T.S.' In fact there is no π^* orbital that the σHOMO can mix with for the cis distortion. It also appears that here the σ-π^* electron transfer is even more important than the normally predominant π-σ^* mixing. The reason for this is as follows. In the flat model, two electrons are present in the π framework. In the optimised calculations, we find that the two carbon 2p atomic orbitals making up this framework contain 1.956 and 1.947 electrons



Energy difference

= 1·9 kcal/mole

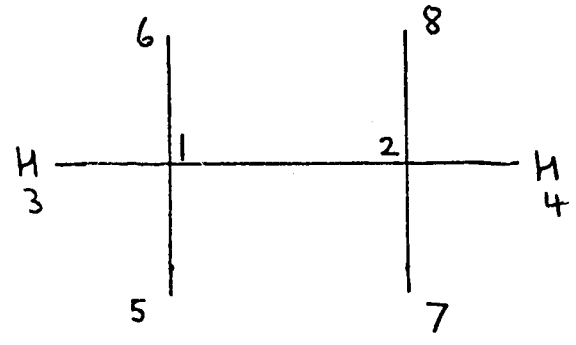


E (Staggered − Eclipsed)

	1	2	3	4	5	6	7	8
1	0.0116459							
2	-0.1155256	0.1115855	-0.1004314					
3	0.0001314	-0.0111302	-0.1271569	-0.0014473				
4	-0.0001356	0.0002253	0.0113454	0.0035356	-0.0004659			
5	0.0002568	-0.0001381	0.0035456	0.0003353	-0.0026562	-0.0004818		
6	-0.0011334	0.0003133	0.0003454	0.0035356	-0.0012941	-0.0026562	-0.0004659	
7	0.0002568	-0.0001381	0.0035456	0.0003353	0.0003568	0.0003438	-0.0026562	-0.0004818
8	-0.0001384	0.0003133	0.0035456	0.0003353	-0.0012941			

0.0194573 Sum of 1-centre energy difference terms.
-1.0433272 Total Energy difference.

Figure 3.16 Energy Difference Matrix For Staggered and Eclipsed Forms of Ethane.



C–C 1·494 Å ; All C–H's 1·210 Å.

(a) Distortion Towards Trans.

C_{ij_0} $i\rightarrow$	6	7	8	9	10	11
1	0.[illegible]1132	-0.[illegible]31208	-0.[illegible]3597	0.[illegible]86922	-0.[illegible]1991	-0.[illegible]41359
2	-1.[illegible]23191	1.[illegible]6165	0.[illegible]13[illegible]	-0.[illegible]2[illegible]	0.[illegible]39[illegible]	-0.[illegible]2734
3	0.[illegible]1	0.[illegible]	-0.[illegible]	0.[illegible]	-0.[illegible]	0.[illegible]
4	0.[illegible]4869	0.[illegible]287676	-0.[illegible]521	0.[illegible]23[illegible]	0.[illegible]14887	-0.[illegible]11764
5	0.[illegible]12	-0.[illegible]1	-0.[illegible]1[illegible]	-0.[illegible]16	-0.[illegible]3[illegible]	0.[illegible]
j_0 6	0.[illegible]94295	-0.[illegible]18952	-0.[illegible]321435	0.[illegible]5[illegible]	-0.[illegible]79212	0.[illegible]1317
↓ 7	-0.[illegible]5[illegible]	-0.[illegible]41332	0.[illegible]3[illegible]	0.11[illegible]93	-0.[illegible]4917	-0.[illegible]5[illegible]
8	.0833[illegible]	[illegible]	0.[illegible]2731	[illegible]	0.[illegible]5329	0.[illegible]3587
9	[illegible]	-.109[illegible]	0.[illegible]2573	-0.[illegible]7[illegible]	0.[illegible]7784	0.[illegible]3[illegible]
10	-0.[illegible]5[illegible]	[illegible]	0.[illegible]7[illegible]	-0.[illegible]9[illegible]	-0.9999[illegible]	0.[illegible]3
11	0.[illegible]7	-0.[illegible]21[illegible]	0.[illegible]31739	-0.[illegible]7[illegible]	-0.[illegible]6917[illegible]	-0.99744773
12	-0.[illegible]1	-0.[illegible]9	0.[illegible]	-0.[illegible]	0.[illegible]	-0.[illegible]2
13	0.[illegible]7[illegible]	-0.[illegible]13[illegible]	0.[illegible]57[illegible]	0.[illegible]22[illegible]	-0.[illegible]2593	0.[illegible]5701
14	0.[illegible]	-0.[illegible]	0.[illegible]	0.[illegible]	0.[illegible]	-0.[illegible]
P_{j_0}	0.99282737	0.96760390	0.03693089	0.01262093	0.00018752	0.00023093
$j_0\rightarrow$	6 HOMO π	7 HOMO σ	8 LUMO σ*	9 LUMO π*	10 σ*	11 σ*
SYMMETRY (C_{2v})	A	{	A_1	} B	A	B

Mixing.

(b) Distortion Towards Cis.

C_{ij_0} $i\rightarrow$	6	7	8	9	10	11
1	-0.[illegible]172	-0.[illegible]43	0.[illegible]622	0.[illegible]2823	0.[illegible]0614	-0.[illegible]4457
2	0.[illegible]498	-0.[illegible]20	-0.[illegible]094	-0.[illegible]96720	-0.[illegible]587	0.[illegible]573
3	0.[illegible]	0.[illegible]	0.[illegible]	-0.[illegible]	-0.[illegible]	-0.[illegible]
4	-0.2414235	-0.[illegible]5	0.[illegible]357	-0.[illegible]12053	-0.[illegible]4200	-0.[illegible]5185
5	0.[illegible]	-1.[illegible]	0.[illegible]	0.[illegible]	-0.[illegible]	0.[illegible]
j_0 6	0.99935765	1.[illegible]4356289	-0.[illegible]7186	0.[illegible]30	-0.[illegible]25[illegible]	0.[illegible]2213[illegible]
↓ 7	0.[illegible]4388517	-0.9996[illegible]	-0.[illegible]3[illegible]12	-0.[illegible]	0.[illegible]51[illegible]	0.[illegible]3[illegible]
8	[illegible]	-0.[illegible]52[illegible]	0.992[illegible]42[illegible]	-1.12[illegible]31[illegible]	0.[illegible]2314[illegible]	-0.[illegible]11[illegible]
9	0.[illegible]3[illegible]	[illegible]0/997	0.12[illegible]8991	0.992[illegible]625	0.[illegible]37[illegible]	-0.[illegible]3359
10	-0.[illegible]3[illegible]	-1.[illegible]0416	0.[illegible]5311	1.[illegible]	-0.99999248	-0.[illegible]8997
11	0.[illegible]83	-0.[illegible]1720	-0.[illegible]9445	0.[illegible]42	0.[illegible]6577	-0.9997[illegible]
12	0.[illegible]	-0.[illegible]	0.[illegible]1	-0.[illegible]	-0.[illegible]	0.[illegible]
13	-0.[illegible]2663	0.[illegible]711	0.[illegible]315[illegible]	0.[illegible]1594[illegible]	-0.[illegible]12[illegible]	0.[illegible]1[illegible]
14	0.[illegible]	0.[illegible]	0.[illegible]	-0.[illegible]	0.[illegible]	-0.[illegible]
P_{j_0}	0.99951077	0.99999675	0.00[illegible]90	0.[illegible]3667	0.[illegible]30	0.[illegible]48869
$j_0\rightarrow$	6 HOMO π	7 HOMO σ	8 LUMO σ*	9 LUMO π*	10 σ*	11 σ*
SYMMETRY (C_{2v})	A	A	B	B	A	A

No HOMO|π| – LUMO|π*| mixing.

Figure 3.17 Matrix of Values For C_{ij_0} and P_{j_0}, For Cis and Trans Distortions to The Flat Ethane Model of Elimination.

in toto, in the eclipsed and staggered forms (again the more stable form has the greater π depopulation). Therefore in this system there is a much less drastic π a.o. depopulation on going to the 'intermediates' than in the previous examples. This means that π-σ^* interactions are not now of overwhelming importance and a mutual electron transfer between π and σ orbitals is involved, including σ-π^* mixing also.

The observation that it is the 2-centre terms that favour the trans form raises an interesting possibility. In the previous examples where the stability of the preferred species was associated with extra *s* character on the atoms in that species, this stability had to arise from greater second order inter-m.o. mixing between filled and unfilled orbitals of the particular flat model, on moving towards the more stable form. This must be so, since there is no other way (e.g. by first order intra-m.o. perturbation) by which extra electron density in a particular atomic orbital (e.g. H_{1s},C_{2s}) can be provided. However a 2-centre destabilisation might be merely the result of bringing the two hydrogens closer together (i.e. the first order change in the energy of the m.o.*s* of the flat model). Now if there were an antibonding interaction between the centres in the flat model, to a first approximation this would increase as the interatomic distance was reduced (the derivation of the Hückel bond order factor theory, for example, implies just this) and similarly if there were a bonding interaction. Therefore in order to determine the qualitative nature, that is the sign, of the first order perturbation energy change associated with the H_3.....H_4 centres on moving towards the two intermediates, we need only look at the sign of this energy term in the flat model. The value of the H_3.....H_4 energy term in the flat model is found to be -.000728 a.u. (i.e. a stabilising term). This

implies that the cis distortion would be of lower energy than the trans distortion. But this is not the case and we therefore deduce that again it is the second order mixing effect (σ-π^* and π-σ^*) which is responsible for the 2-centre stabilisation, which is in turn responsible for the preference for a trans distortion.

(b.) We will now investigate a variety of flat models (and their distorted forms) which do not possess the elements of symmetry previously exploited (i.e. a C_2 or σ_v symmetry element) in the two transition states/intermediates. Obviously HOMO-LUMO mixing will not be so strictly symmetry-contolled in the two distortions, in that the interaction term, H'_{iojo}, will not be zero or non-zero depending on the symmetries of orbitals ϕ_{io} and ϕ_{jo}. But although H'_{iojo} will not necessarily be zero, it should still be quantitatively different for the two distortions. In other words, although symmetry restrictions have been lifted, HOMO-LUMO interactions should still favour the trans distortions.

The geometries of the four flat models that were studied are given in Figure 3.18. They represent 'flat' T.S.s in the following four reactions.

(a.) Elimination of water from ethanol.

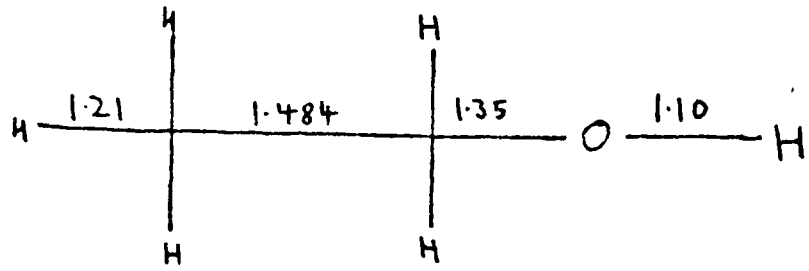
(b.) E2 attack of hydride (base) on ethane.

(c.) E2 attack of hydroxide on ethane.

(d.) E2 attack of hydride on ethanol.

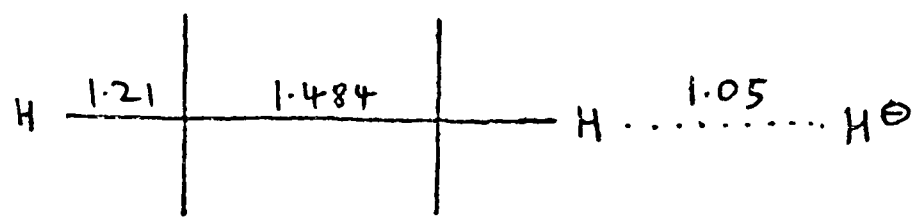
For the distortions, the CH_2-CH_2 central framework in all cases was undisturbed. For cis distortions, all other atoms were moved above the plane by 0.1 a.u. For trans distortions, atoms at one end

(a.)



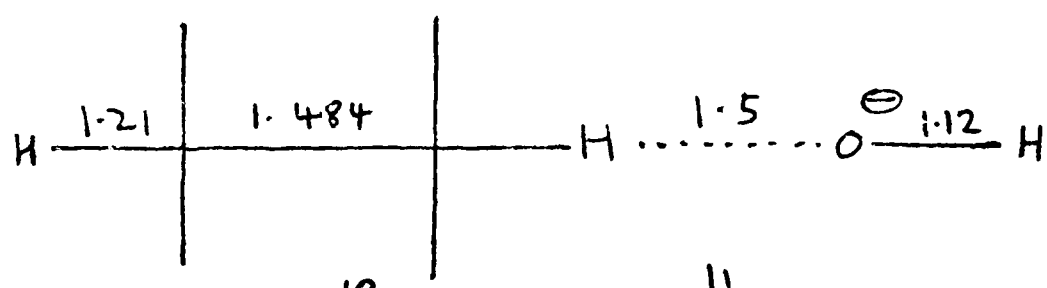
	9 HOMO π	10 HOMO σ	11 LUMO σ*	12 LUMO π*
P_{jo} (CIS)	·9991	·9977	·0008	·0024
P_{jo} (TRANS)	·9967	·9992	·0035	·0013 ‖

(b.)



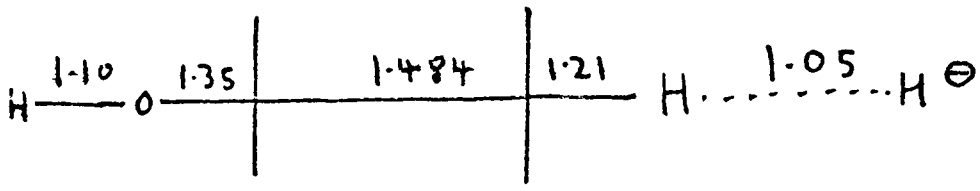
	7 HOMO π	8 HOMO σ	9 LUMO π*	10 LUMO σ*
P_{jo} (CIS)	·9995	·9995	·0007	·0003
P_{jo} (TRANS)	·9990	·9986	·0015	·0009 ‖

(c.)



	10 HOMO π	11 HOMO σ	12 LUMO σ*	13 LUMO π*
P_{jo} (CIS)	·9995	·9994	·0002	·0007
P_{jo} (TRANS)	·9985	·9982	·0014	·0021 ‖

(d.)



	10 HOMO π	11 HOMO σ	12 LUMO π*	13 LUMO σ*
P_{jo} (CIS)	·9998	·9995	·0009	·0003
P_{jo} (TRANS)	·9994	·9991	·0013	·0008 ‖

(All bond lengths are in Å; all C—H's are of the same length)

Figure 3.18. Occupancies of MOs in Distorted Forms of Various Elimination Models.

of the CH_2-CH_2 chain were raised by 0.1 a.u. and atoms at the other end were lowered by the same amount. The base.....H distances used were greater, by $\sim$·15 Å, than the optimum distances found in the OLD-MINDO calculations (see Figure 3.14). This is to compensate for the previously noted shortening of bonds that are being broken/formed during reactions involving anionic species, when MINDO/2 is used (c.f. S_N2' intermediates).

The values of P_{jo} for the 2 HOMOs (σ&π) and 2 LUMOs (σ^*&π^*) are also given in Figure 3.18. In all cases, these four orbitals were found to be grouped together, in terms of their eigenvalues. Also in all cases, mixing between these orbitals were the major interactions, especially so for the trans distortions. For the three models in which a base is present, both the π-σ^* and σ-π^* mixings are much greater in the trans distortion. For ethanol, the overall electron transfer to σ^* and π^* strongly favours the trans distortion, but in this case the σ-π^* mixing is greater in the cis case. Because of the crudity of these models, further quantitative information will be somewhat unreliable and will not be derived. Nevertheless the application of considerations of HOMO $\{\pi, \sigma\}$ - LUMO $\{\sigma^*, \pi^*\}$ interactions as a predictive tool now appears to be beyond doubt, even in systems where symmetry does not distinguish between the transition states.

Further symmetric reactions, in sections 7 and 9, will be dealt with merely by inspection of the symmetries of the HOMO σ/π and LUMO σ^*/π^* orbitals in the flat and/or rotated models that are appropriate. Not only will this give further credibility to the HOMO-LUMO theory, but it will also widen its scope so as to include both acyclic and pericyclic reactions. Of course, a HOMO-LUMO theory of the latter was expounded some time ago by Fukui (1971) and has been described in the introduction. However the present approach, in terms of flat and rotated models, will in many reactions lead to species

being considered different from those of Fukui, and in a more general way.

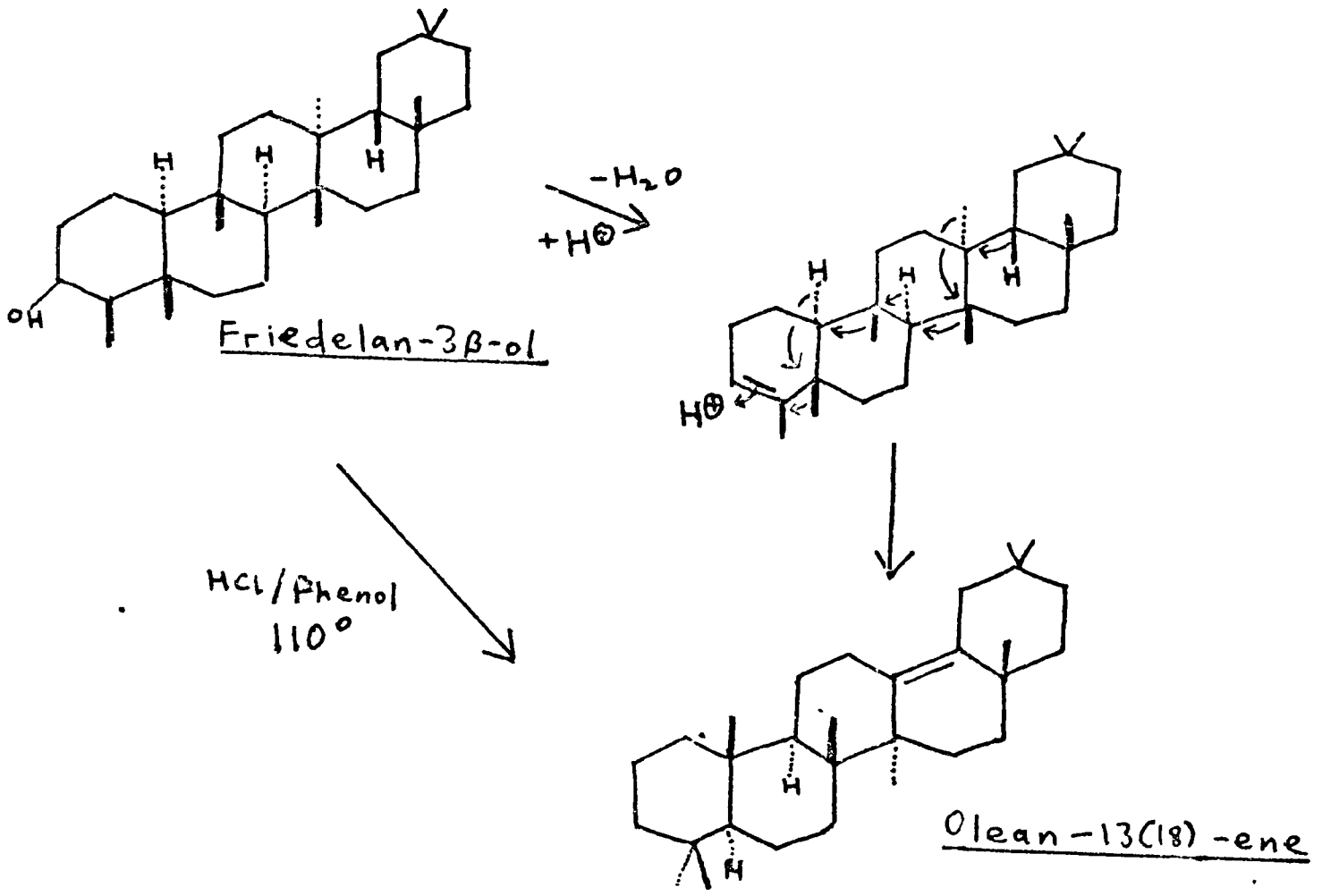
7. The Backbone Rearrangement.

The essential step of a backbone rearrangement reaction has been given in Figure 1.9. The particular reaction studied by Corey and Ursprung (1955) was the fascinating multi-group rearrangement of Friedelan-3β-ol to olean-13(18)-ene, shown in Figure 3.19(a). All hydrogen and methyl migrations proceed suprafacially with inversion at the carbons which are attacked. A model for this reaction therefore, is the intramolecular interconversion of two 1-propyl cations, by the alternative pathways shown in Figure 3.19(b).

A flat model of intermediate geometry between the two T.S.s was set up, the details of which are given in Figure 3.20(a). The bond lengths used were intuitive. In order to ensure that bond length changes did not affect the conclusions, the positions of the migrating hydrogens in the plane were varied. The conclusions were found still to hold. The symmetries and orbital energies of the orbitals about the filled/unfilled borderline are given in the Figure. We would predict that the anti T.S. is favoured, in line with experiment, since only by anti distortion can the HOMO$\left\{\begin{matrix}\sigma\\ \pi\end{matrix}\right\}$ interact with the LUMO$\left\{\begin{matrix}\pi\\ \sigma^*\end{matrix}\right\}$.

A rotated model was also studied for this system, for comparison with the flat model. This model, which is shown in the Figure can be obtained simply by rotating the end CH_2 groups of the flat model, through 90^o. The resulting borderline m.o.s are described in the table. As in the flat model both decisive HOMO-LUMO mixings can only occur for rotations leading to the anti T.S.. However for this model

(a.)



(b.)

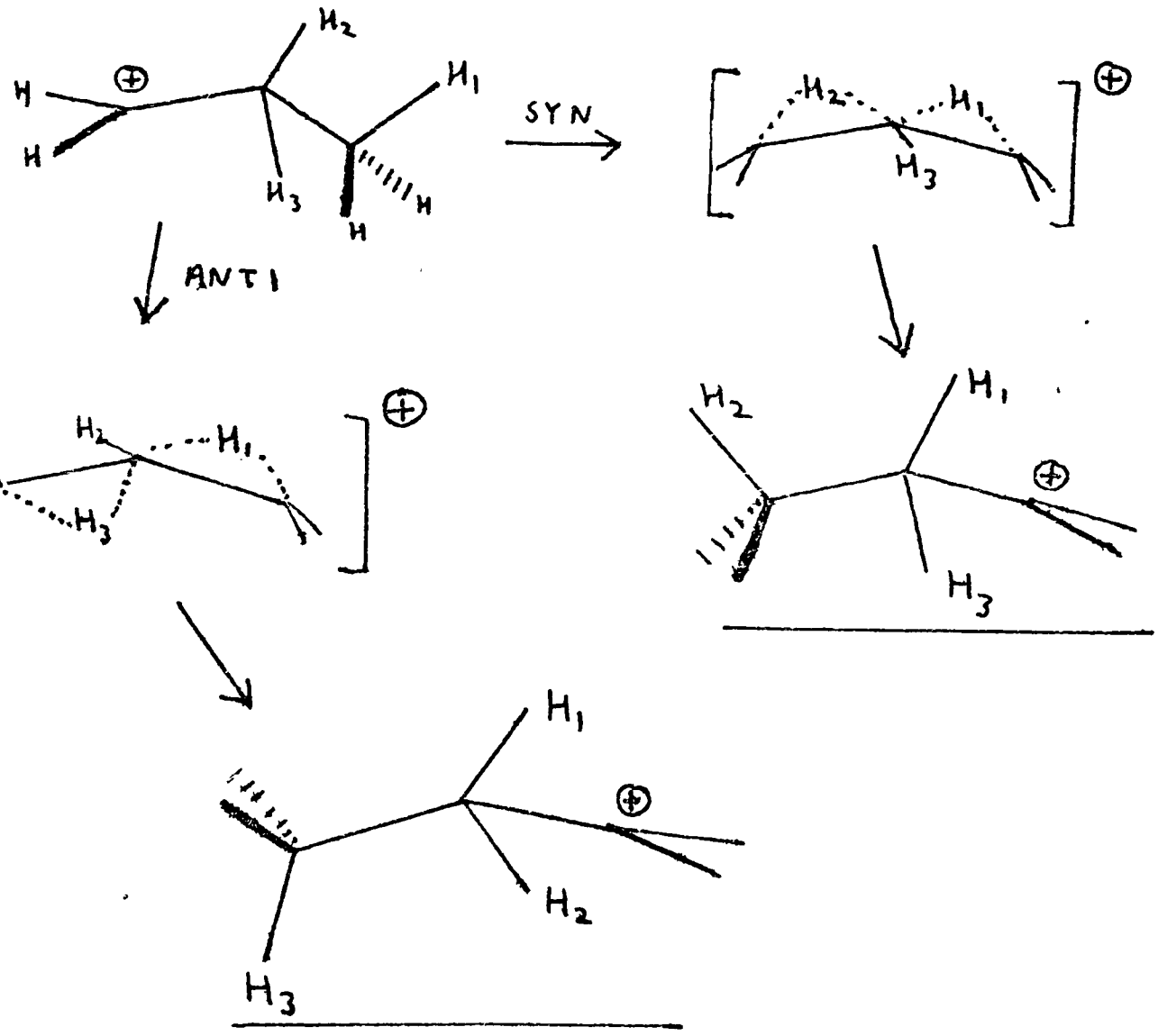
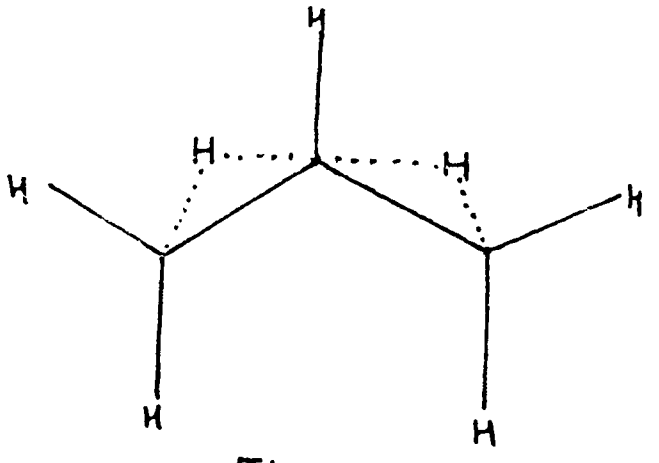


Figure 3.19 Backbone Rearrangement of Friedelan-3β-ol and a Model of the Migration Step.

(a.)



FLAT

All C–H bond lengths = 1.21 Å

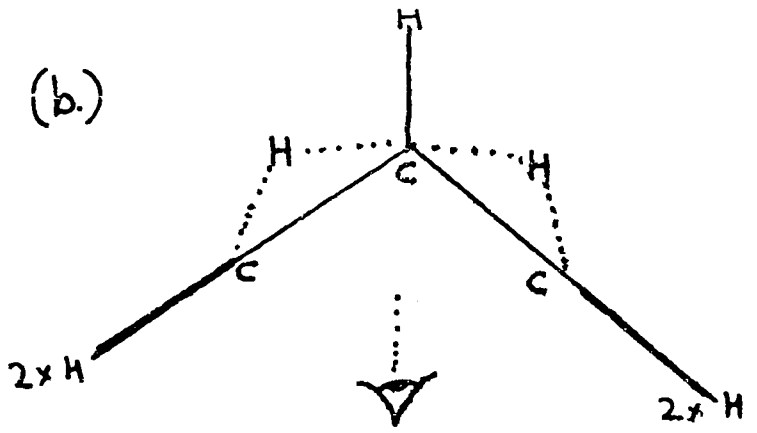
All angles of the allyl framework = 120°

C–C bond lengths = 1.453 Å

Orbital Number.	$e^{S.C.F.}_{MINDO}$	Type	Symmetry C_2 (ANTI)	Symmetry σ_v (SYN)
8	−.636	HOMO σ	A	A
9	−.509	HOMO π	S	A
10	−.219	LUMO π*	A	S
11	−.205	LUMO σ*	S	S

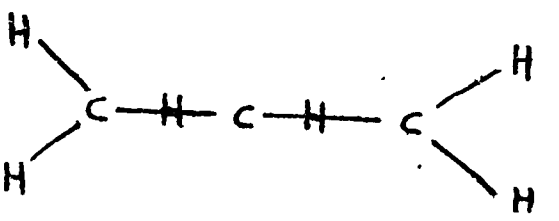
$\therefore C_2$

(b.)



ROTATED

≡



All angles and bond lengths as above.

Orbital Number.	$e^{S.C.F.}_{MINDO}$	Type	Symmetry C_2	Symmetry σ_v
7	−.677	HOMO π	S	A
8	−.560	(HOMO−1) σ	S	S
9	−.546	HOMO σ	A	A
10	−.293	LUMO π*	A	S
11	−.216	LUMO σ*	S	S

$\therefore C_2$

Figure 3.20 Flat and Rotated Model Intermediates For The Migration Step of The Backbone Rearrangement.

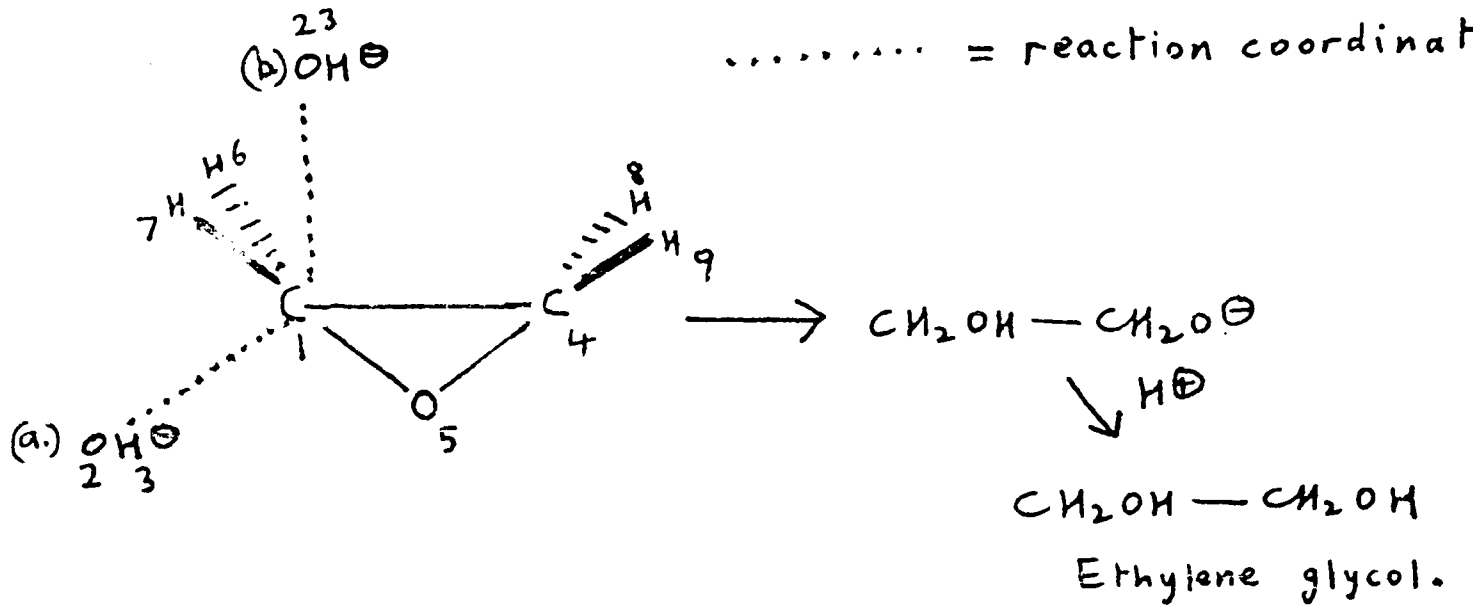
we may go a stage further in our analysis. We have a situation with respect to the HOMO σ orbital which we have already found with the S_E2^1 rotated model, in that below the HOMO σ there lies another σ orbital of opposite symmetry but with a very similar eigenvalue. Thus this σ m.o. can mix with the LUMO π* in the syn distortion only and strongly counterbalance the effect of HOMO σ - LUMOπ* interaction in the anti distortion. We would therefore predict that the differences in the syn and anti transition states are related more to the HOMO π - LUMO σ* mixing of the rotated model, than to the more favourable (in terms of energy gap) HOMO σ- LUMOπ* electron transfer, as was found to be the case in the S_E2^1 intermediates.

Before treating pericyclic reactions by the above model(s), we will conclude our survey of acyclic reactions with a detailed study of an S_N2 type reaction.

8. A Study of the Reaction of Hydroxide Ion with Ethylene Oxide.

This reaction was studied, as it is described as an example of an S_N2 type mechanism (see Gould (1959)), for which we had previously been unable to derive simple T.S.s using $CH_5^{\ominus}$. It also allows one to observe the effect that another main atom has on the reaction and possibly to determine whether it plays any part in stabilising one T.S. more than another.

The OPTMO program was amended to allow construction of an optimised total reaction pathway (see Appendix 1, and Chapter 1 for details). The reaction coordinate in this case was the oxygen....carbon distance of the bond being formed (see Figure 3.21). This distance was varied by fixed amounts and the geometry was recptimised at each point. In



..... = reaction coordinate

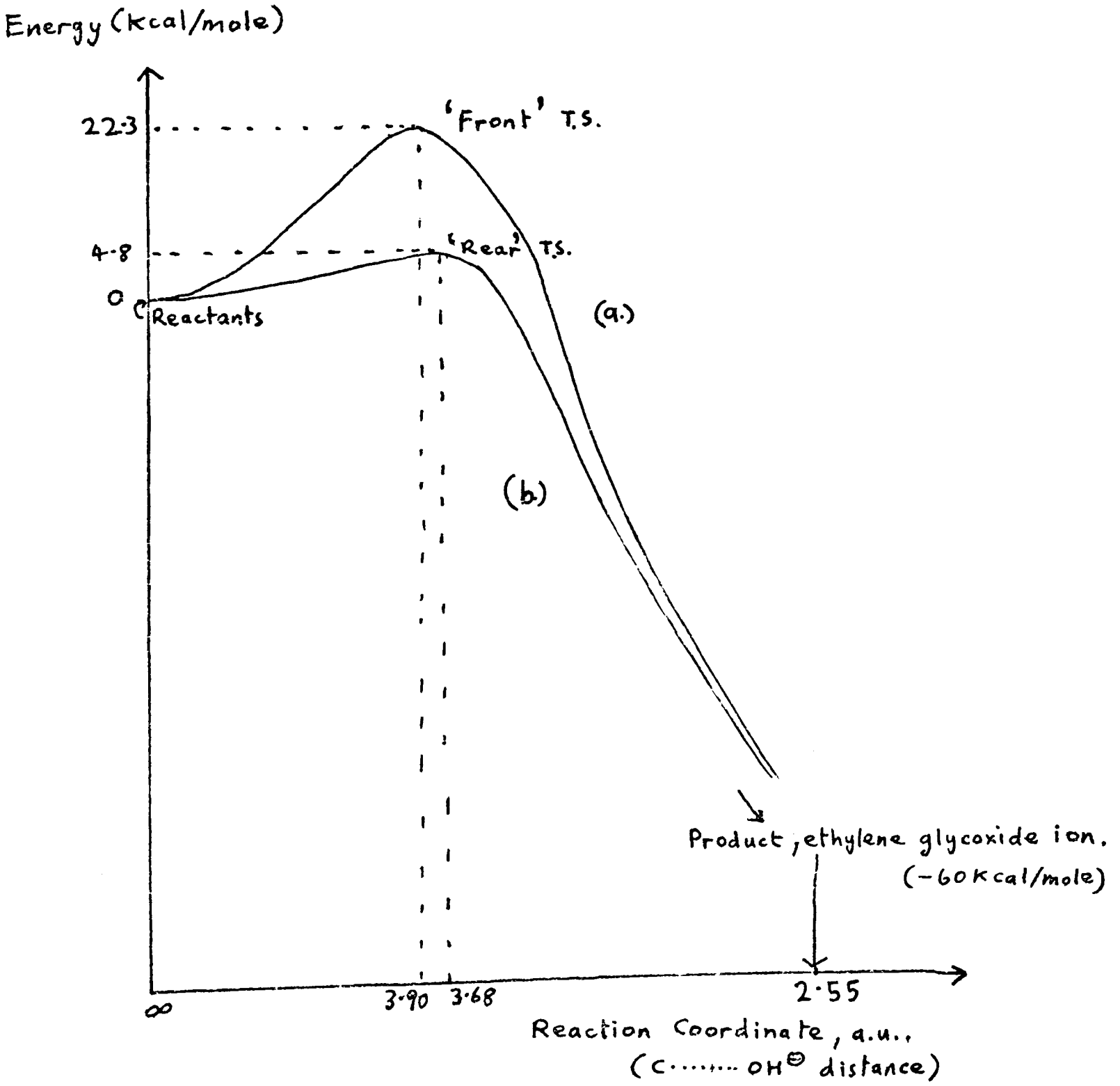
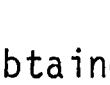


Figure 3.21 Energetics of The 'Front' and 'Rear' Attacks of Hydroxide Ion on Ethylene Oxide.

fact it is theoretically possible (but rarely achieved for one reason or another), to roughly construct the whole of a reaction pathway in one computer job! From the plot of energy versus reaction coordinate, the value of the reaction coordinate at the T.S. is deduced and the geometry is then totally optimised (10^{-4} gradient) at this point. It is also necessary to plot the optimised coordinates of the atoms at points along the reaction pathway to check that the correct reaction is occurring.

The hydroxide ion was allowed to approach from directions (a.) and (b.), as shown in Figure 3.21, corresponding respectively to 'front' and 'rear' attack (in relation to the bond being broken). Of course the particular direction shown is only applicable for the initial stages of the reaction, since the C...$OH^{\ominus}$ distance alone is fixed and the orientation of this incipient bond can freely change in relation to the other bonds, with the restriction that the hydroxide ion must remain in the same plane as the  atoms. Two energy profiles were thus obtained and are given in Figure 3.21, together with the main details of the transition states. The geometries of the T.S.s themselves can be seen in Appendix 2 (numbers 14 & 13). The optimised geometry of ethylene oxide is also shown (number 15).

The calculations predict the rear attack to be preferred by 17.5 k.cal/mole. The transition states differed by ~·1.Å in the value for the reaction coordinate. It was possible that other differences between the two T.S.s might be caused mainly by this difference in bond length. In order to investigate this possibility a point was optimised along the 'front' attack pathway in which the C.....$OH^{\ominus}$ distance was the same as that in the 'rear' attack T.S. (3.68 a.u.). It was found that the analysis to be

described, which refers to the two transition states, was unchanged when this geometry replaced the 'front' T.S.. Hence we can discount the idea that variations in this bond length affect our conclusions.

The energy difference matrix for the two T.S.s is given in Table 3.19, where the atoms are numbered as shown in the Figure. One observes that here it is the 2-centre energy difference terms that stabilise the 'rear' T.S. But more importantly one sees that the O.....O energy term favours the less stable 'front' T.S. In other words there is <u>less</u> repulsion between the oxygen atoms in the 'front' T.S., (the calculations show that the O.....O term is repulsive in both transition states). The major stabilising 2-centre term between 'non-bonded' atoms in the 'rear' T.S. is the $O_{(2)}$..... $C_{(4)}$ term. In fact, if one sums the 1-centre difference terms for the main atoms and the 2-centre difference terms for bonds between the main atoms, both these figures favour the less stable 'front' T.S. In terms of the main atoms it is the <u>O.....C</u> term alone that can account for the stability of the rear T.S..

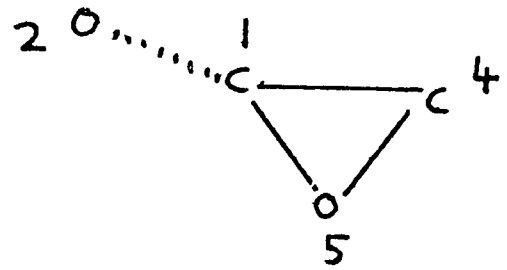
The above conclusion emphatically answers the query posed at the beginning of this section, concerning the part played by the extra main atom. Not only does it play a part, it plays the major part. This obviously implies that it is misleading to consider the reaction as involving essentially three main atoms. The choice is not now between a linear or bent T.S. (see Figure 3.22 (a.)), but between the T.S.s shown in Figure 3.22(b.). These systems cannot be treated by the <u>simple</u> HMO theory as it cannot distinguish between O and C atoms, which means that both T.S. models would be of equal energy within that context.

It will be remembered from the discussion concerning the conformations of ethane in the section on elimination reactions,

E (REAR T.S. − FRONT T.S.)

	1	2	3	4	5	6	7	8	9
1	-0.0741995								
2	0.0129229	0.0057301							
3	-0.0034621	-0.0029348	0.0076631						
4	-0.1512297	-0.0594504	0.0092316	0.1459156					
5	0.1955923	0.0117757	-0.0035367	-0.1005121	-0.0065312				
6	0.0073348	-0.0077713	0.0039625	-0.0039155	0.0014691	0.0048874			
7	0.0073347	-0.0177726	0.0089626	-0.0039454	0.0014691	-0.0027311	0.0048878		
8	0.0053176	0.0195012	-0.0104746	-0.0177185	0.0057959	0.0002665	-0.0009249	-0.0014654	
9	0.0053177	0.0095813	-0.0054745	-0.0177183	0.0057959	-0.0009249	0.0032654	0.0007623	-0.0014655

0.0183937 Σ1-centre energy differences.
-0.0127824 Total energy difference.



(a.) Σ1-centre energy difference terms for main atoms
= 0·01093

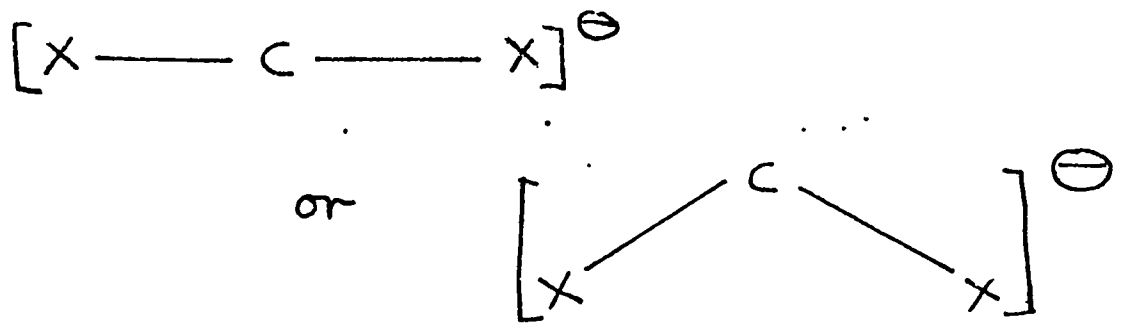
(b.) Σ2-centre energy difference terms for bonds between main atoms = 0·00077

Main Atom Terms (Differences).

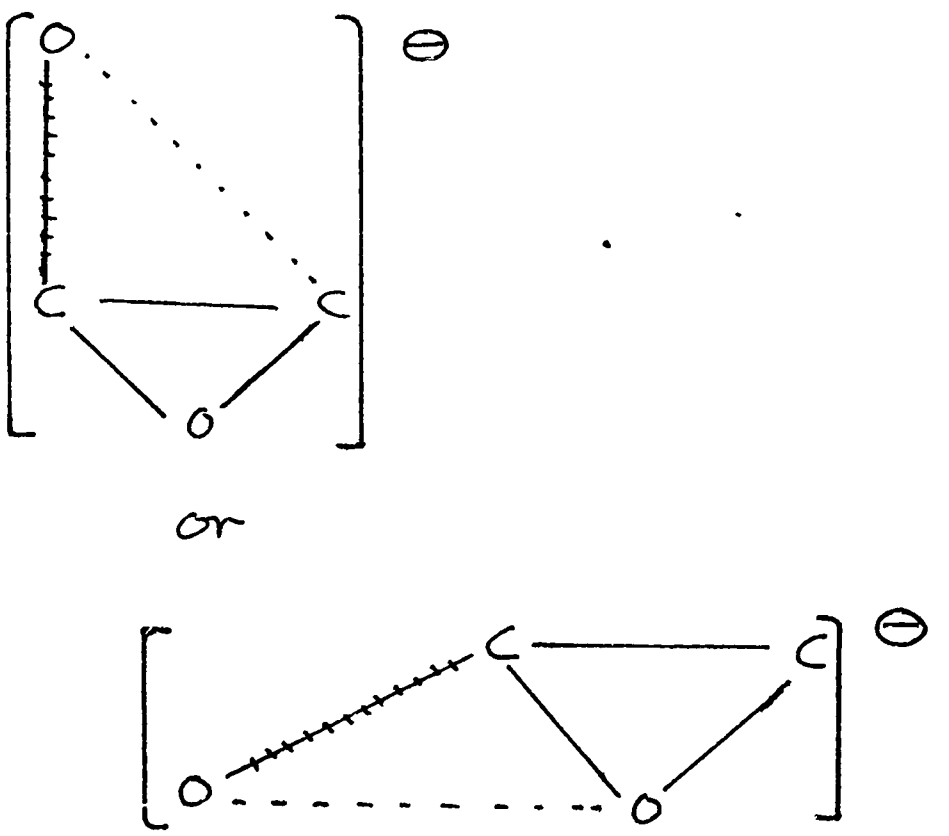
(a.) 1-centre, main atoms	0·01093
(b.) 2-centre, main atom bonds	0·00077
(c.) $O_2 \cdots\cdots O_5$ term	0·01178
	0·02348
(d.) $O_2 \cdots\cdots C_4$ term	−0·05949
	−0·0360

Table 3.19 Energy Difference Matrix (REAR-FRONT) For T.S.s in Reaction of $OH^{\ominus}$ With Ethylene Oxide.

(a.) <u>S_N2</u>



(b.)



(c.) <u>Intermediate Model.</u>

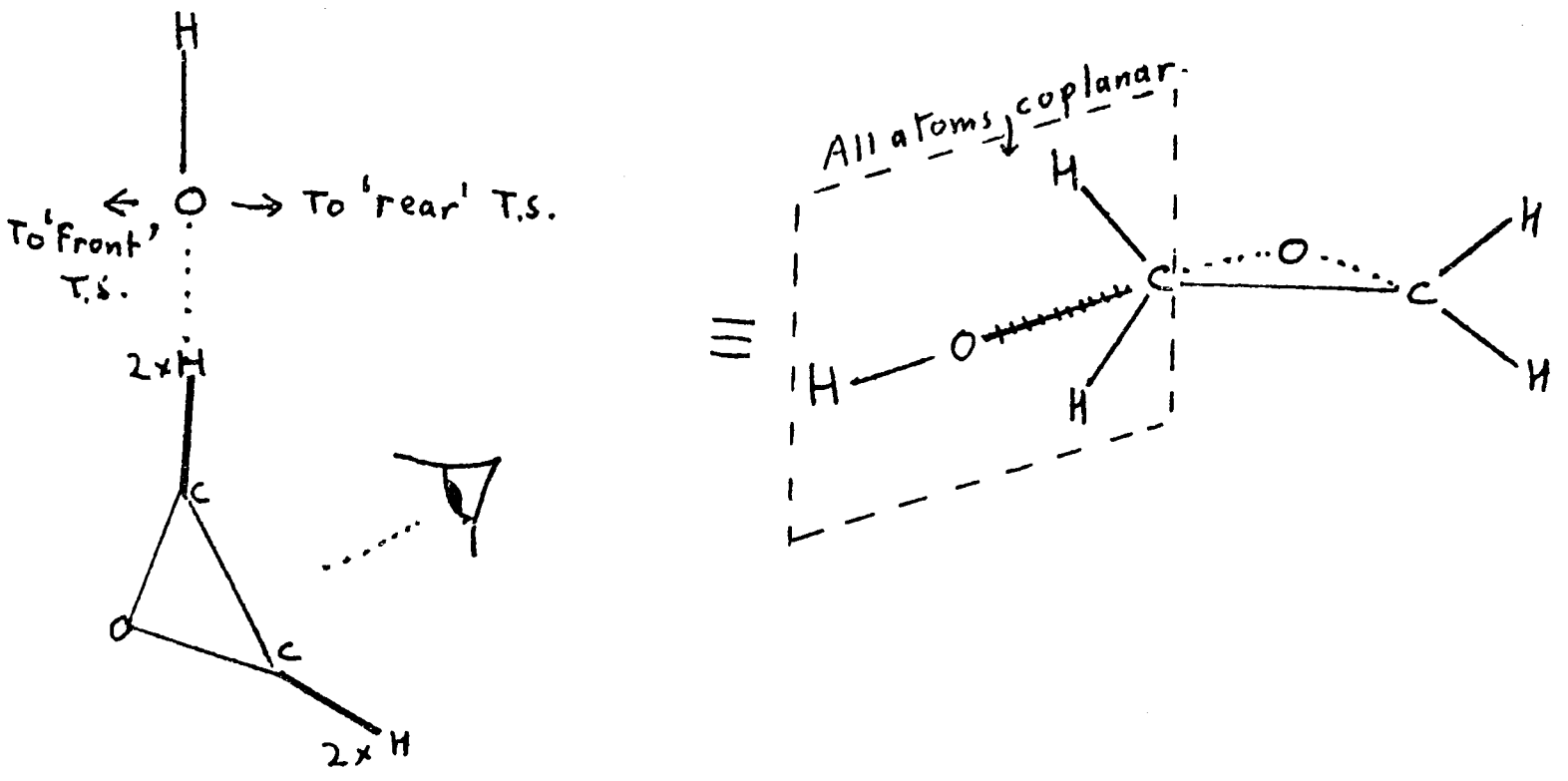


Figure 3.22 Simple Models For The $OH^{\ominus}$ + Ethylene Oxide Reaction

that 2-centre stabilisation can arise from intra- or inter- m.o. effects (i.e. first or second order perturbations). In that system, the second order effect seemed to be decisive. We will now investigate the situation in this reaction, using our deductions from that analysis as a guide.

First we must derive an intermediate model between the two T.S.s, in line with previous analyses. The T.S.s themselves differ only in the orientation of the $OH^{\ominus}$ group with respect to the epoxide ring, (Figure 3.22 (b.)). At some intermediate position the incipient $C_{(1)}\cdots\cdots OH^{\ominus}$ bond and the two $C_{(1)}$-H bonds are coplanar (Figure 3.22 (c)). Distortion of the $OH^{\ominus}$ group out of this plane would lead to either of the two T.S.s, depending on the direction of distortion. Thus the intermediate model was obtained by keeping the C.....O bond and the two C-H bonds coplanar, with the C....O distance fixed at 3.8 a.u. (an average value for the two T.S.s) as shown in the Figure. All other bond angles and bond lengths were allowed to optimise. The total energy breakdown matrix for the resulting species is given in Table 3.20.

It was deduced in the ethane discussion that in order to determine the qualitative nature of the first order perturbation energy change associated with changing an interatomic distance in a molecule, one should look at the sign of the energy term between the centres in the undistorted model. It is seen that the $O_{(2)}\cdots C_{(4)}$ term is bonding (- .0527 a.u.) which suggests that the first order perturbation energy change to this term will favour the 'rear' T.S., where these centres are much closer than in the 'front' T.S. Whether it accounts for the major part of the observed 2-centre difference term can only be judged when we have also investigated the second order change,

TOTAL ENERGY MATRIX (ONE & TWO CENTRE TERMS)

	1	2	3	4	5	6	7	8	9
1	-3.8719183								
2	-4.0555436	-11.3182649							
3	-2.3831464	-2.5219797	-3.3228156						
4	-4.4435192	-1.6525612	-0.0092633	-3.6634594					
5	-4.4519197	-0.1227135	-0.0114448	-1.0761912	-10.9985276				
6	-1.3981345	-0.1345982	-0.0105625	-0.0172555	-0.0025166	-0.3461521			
7	-1.3981345	-0.1345982	-0.0105626	-0.0172555	-0.0025166	-0.0296244	-0.3461521		
8	-0.0993749	-0.0225317	-1.2236573	-0.4626285	-0.0490697	-0.0021494	-0.0045692	-0.1246451	
9	-0.0993749	-0.0225317	-1.0136573	-0.4626285	-0.0490697	-0.0045692	-0.0021494	-0.0272334	-0.1246451

-31.41355232 Σ 1-centre energies.
-35.26447568 Total energy, a.u..

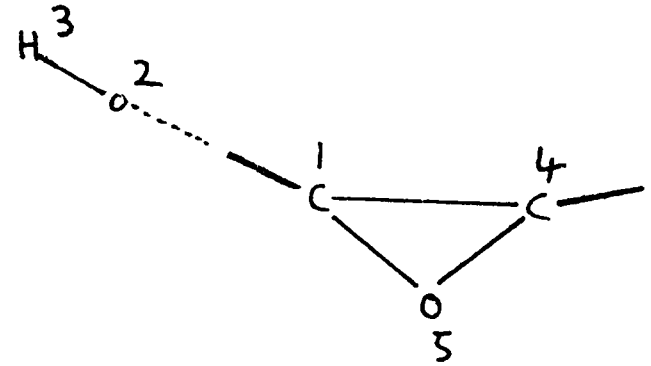


Table 3.20 Energy Breakdown Matrix For Intermediate Model in The $OH^{\ominus}$ + Ethylene Oxide Reaction.

due to orbital mixing.

To do this, the intermediate model was distorted by moving the $OH^{\ominus}$ group 0.1 a.u. above and below the plane formed by the C.....O and C-H bonds. The values of P_{jo}'s for these distortions are given in Table 3.21. As can be seen, what little orbital mixing that occurs, is virtually the same for the two distortions, if anything favouring the 'front' distortion. In both cases there is no electron transfer from the HOMO (orbital 13), and orbital 9 transfers the greatest amount (mainly to orbital 15). Thus we can definitely say that second order mixings in general, and HOMO-LUMO mixings in particular, play no significant role in producing the observed relative stabilisation of .00113 a.u. in the energy of the 'rear' distorted form. We conclude therefore that the 2-centre stabilisation arises from first order perturbation energy changes to the m.o.s , unlike our other examples. (N.B. We would not expect HOMO-LUMO mixing (13→14), as orbital 13 is a 'π' orbital, in that the species has a mirror plane, containing the epoxide ring atoms, which leads to 6 π and 15 σ orbitals, of which orbital 14 is of the latter type. The π orbitals are given in the table and on symmetry grounds, the distortions of interest cannot mix them with the σ orbitals. This does not rule out 11,12 → 14,15 interactions, which though small, are not zero).

Hence the 'S_N2 type' reaction is found to be fundamentally different to our previous studies. Also it has been shown not to be a 'pure' S_N2 reaction in that the supposedly 'non-participating carbon' was found to play the major role in terms of conformational preference. This shows the distinct advantage of the energy and orbital energy analysis, which not only enables one to find the origins of conformational preference (in relation to the theoretical method used), but also is not prejudiced by superficial similarities

Orbital Number			P_{jo} (REAR)	P_{jo} (FRONT)
1			1·0	1·0
2			1·0	1·0
3			1·0	1·0
4			1·0	1·0
5	(π)		1·0	1·0
6			1·0	1·0
7			1·0	1·0
8	(π)		1·0	1·0
9			0·99985	0·99985
10	(π)		1·0	1·0
11			0·99998	0·99998
12			0·99997	0·99997
13	(π)	HOMO.	1·0	1·0
14		LUMO.	0·000010	0·000010
15			0·000145	0·000148
16	(π)		0·0	0·0
17			0·000042	0·000039
18	(π)		0·0	0·0
19			0·0	0·0
20			0·0	0·0
21			0·0	0·0

Table 3.21 Occupancies of MOs After 'Front' and 'Rear' Distortions of $OH^{\ominus}$.

between reactions.

9. Pericyclic reactions

This section will be a brief study of pericyclic reaction types, in terms of our previous discussions. It will be useful to present first the major conclusions of the acyclic work. These can be summarised as follows.

(1) The conformational preference in stereospecific acyclic reactions may have its origin in either 1-centre or 2-centre energy stabilisation in the preferred species.

(2) One can set up symmetrical models intermediate between the two (or more) species. On distorting these models towards the two T.S.s/intermediates, one finds that in all cases (except $OH^{\ominus}$ + ethylene oxide) it is the greater second order perturbation energy change associated with inter-m.o. mixing that is the cause of stabilisation in the distorted form leading to the preferred molecule.

(3) In particular, the mixings of importance are HOMO π - LUMO σ^* and HOMO σ- LUMO π^*. For one or more of a variety of reasons (e.g. close σ levels, excess 'π' electron density in intermediate model, energy gap etc.) the former is a more reliable guide to the preferred distortion and should be used when making predictions.

(4) The above mixings are orbital symmetry-controlled. Hence consideration of the relative symmetries of these two pairs of decisive m.o.s , with respect to the symmetry elements preserved during the distortions, forms the basis for explaining and predicting reaction preference.

(5) When one considers intermediate models for reactions not

involving identical incoming and departing groups, HOMO-LUMO mixings are not symmetry-controlled (i.e. they are not zero or non-zero, depending on the distortion). However one still finds that HOMO-LUMO electron transfer is decisive (again, with the exception of the $OH^{\ominus}$/epoxide system) and is greater in the distortion to the preferred species (as favoured by experiment).

(6) The 'essential' part of the T.S./intermediate appears to begin and end at the (partially)-bonded atoms attached to the intervening π system. Thus the base is <u>not</u> an essential part of the T.S. in the E2.

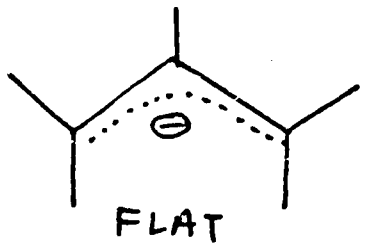
(7) When there are groups attached to two centres in this 'essential' part of the species, they cannot be assumed to be non-participating. Thus in the reaction of hydroxide ion with ethylene oxide, the second CH_2 group plays a major role in energy stabilisation of the preferred 'rear' T.S. This may therefore invalidate the above type of analysis.

We may now test out these axioms, derived from the acyclic studies, on pericyclic systems and determine whether our resulting predictions agree with the known experimental data.

(a.) <u>Electrocyclic Reactions</u>.

For electrocyclic reactions, the reactant and product <u>are</u> the flat and rotated models, in the sense used in the sections on acyclic reactions (e.g. allyl and cyclopropyl, c.f. Figure 3.23). For this reaction type, we shall use the ab initio m.o.s which were obtained for cis-butadiene, allyl cation and allyl anion (see section 1). The nature and symmetries of the borderline m.o.s are given in the Figure.

(a) Allyl anion.



Cyclopropyl anion.



Orbital Number	Type	$e^{S.C.F.}_{ATMOL}$	Symmetry σ_v	Symmetry C_2	
(9	(HOMO-1) σ	−0.263	S	)	
10	HOMO σ	−0.251	A		
11	(HOMO-1) π	−0.177	S	A	∴ C_2
12	HOMO π	−0.024	A	S	
13	LUMO π^*	0.474	S	A	
14	LUMO σ^*	0.653	S		
(15	(LUMO+1) σ^*	0.700	S	)	

(b) Allyl cation.

Orbital Number	Type	$e^{S.C.F.}_{ATMOL}$	Symmetry σ_v	Symmetry C_2	
9	(HOMO-1) σ	−0.838	A		
10	HOMO σ	−0.803	S		
11	HOMO π	−0.690	S	A	
12	LUMO π^*	−0.259	A	S	
13	(LUMO+1) π^*	−0.028	S	A	∴ σ_v
14	LUMO σ^*	0.142	S		
15	(LUMO+1) σ^*	0.154	S		

(c) Butadiene (cis).

Orbital Number	Type	$e^{S.C.F.}_{ATMOL}$	Symmetry σ_v	Symmetry C_2	
12	(HOMO-1) σ	−0.539	A		
13	HOMO σ	−0.518	S		
14	(HOMO-1) π	−0.482	S	A	
15	HOMO π	−0.354	A	S	
16	LUMO π^*	0.118	S	A	
17	(LUMO+1) π^*	0.293	A	S	
18	LUMO σ^*	0.375	S		
19	(LUMO+1) σ^*	0.431	S		

∴ C_2

Figure 3.23 Details of The ATMOL MOs of Flat Models For Electrocyclic Reactions.

It can be seen that for the allyl anion, both HOMO-LUMO pairs (i.e. π/σ^* and σ/π^*)can only mix for the C_2 distortion, leading to the prediction that the conrotatory T.S. will be of lower energy, as is found experimentally. However in the other systems, the two mixings give different predictions. The more reliable π/σ^* interaction (c.f. above axioms) in both cases is only allowed for the experimentally-correct distortion (σ_v in allyl cation → disrotatory T.S., C_2 in cis-butadiene → conrotatory T.S.). If there is a <u>net</u> transfer of electron density from the π a.o.s to the σ a.o.s on distorting the flat species, as was the case in all the acyclic models we studied, this term will be dominant. We would have to locate the transition states or perform calculations on distorted species to be sure that this is in fact so.

On investigating the m.o.s a little further, we will be able to confirm our predictions for the latter examples. In the unlikely event that the π/σ^* and σ/π^* mixings cancel out for the two distortions, we must then observe the natures of the (HOMO-1)σ and (LUMO + 1)σ^* orbitals. (N.B. These are more appropriate than the corresponding π m.o.s because of energy gap considerations and for other reasons which will be given in the next section). Their symmetries and eigenvalues are given in the Figure ((b) and (c)). It can be seen that both these pairs of m.o.s can only interact with the HOMO π and LUMO π^* for the 'experimentally-correct' distortions, σ_v for allyl cation, C_2 for cis-butadiene. Thus even if the HOMOπ-LUMOσ^* electron transfer is not decisive, these lesser secondary effects will contribute to the required stabilisation of the preferred reaction mechanism. Or put differently, there are more second order contributions, by way of orbital mixing, to the stabilisation of the allowed mode of electrocyclisation than there

are to the forbidden mode (i.e. 2 to 0 for the allyl anion and 3 to 1 for the allyl cation and butadiene).

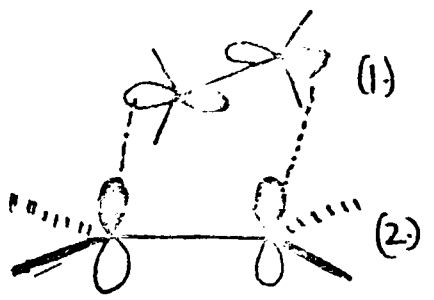
(b) Cycloadditions

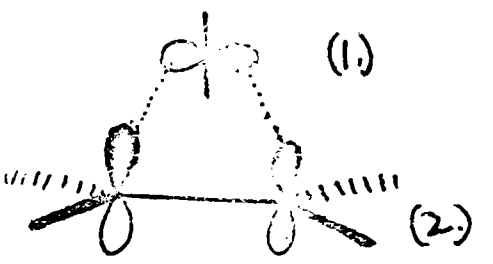
The concerted dimerisation of ethylene to give cyclobutane can be considered to proceed via Hückel or Möbius T.S.s (see Figure 3.24). The mobile four electrons are most stable in the Möbius T.S. (see Chapter 1). We require a model which can be converted into the transition state geometries while maintaining different elements of symmetry. The rotated model in Figure 3.24 is such a species and a MINDO/2 calculation was performed on this species with the geometrical parameters shown. The bond angles and bond lengths in each ethylene moiety are the OPTMO-derived values for an isolated ethylene molecule. The C....C distance of 2.12 Å was chosen to represent a point some distance along the reaction pathway, when the rotations have been performed.

The nature and symmetries of the borderline m.o.s are given in the Figure. The π a.o.s are the four $2p_z$ a.o.s on the carbons and the two antisymmetric combinations of hydrogen 1s a.o.s on the lower ethylene group, in the diagram of the rotated model. We see that C_2 distortion, leading to the Möbius T.S., allows both HOMO-LUMO mixings of importance ($\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$) to occur.

(c) 1,3 Sigmatropic Shift.

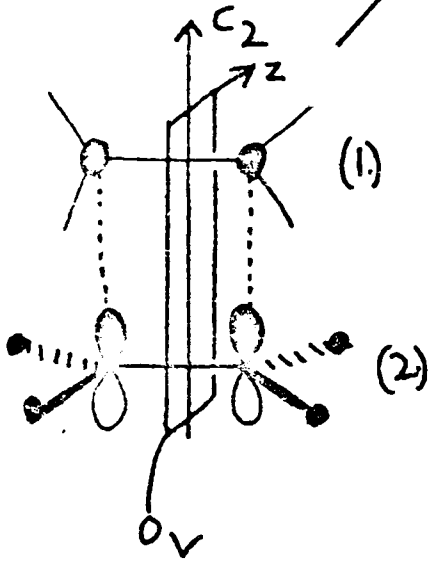
As a model for a 1,3 sigmatropic shift, we will study the rearrangement of propene, which can proceed via a suprafacial or antarafacial shift of the hydrogen (see Figure 3.25 and note the difference in the atomic spatial arrangement that results from the two pathways). As in the backbone rearrangement we have two similar models that can be used to study distortions towards the T.S.s.



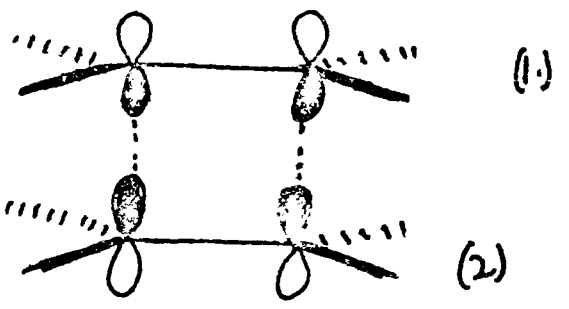


Möbius T.S., 4 electrons
– aromatic.

Rotate (1.), maintaining C_2



Rotate (1.), maintaining σ_v.



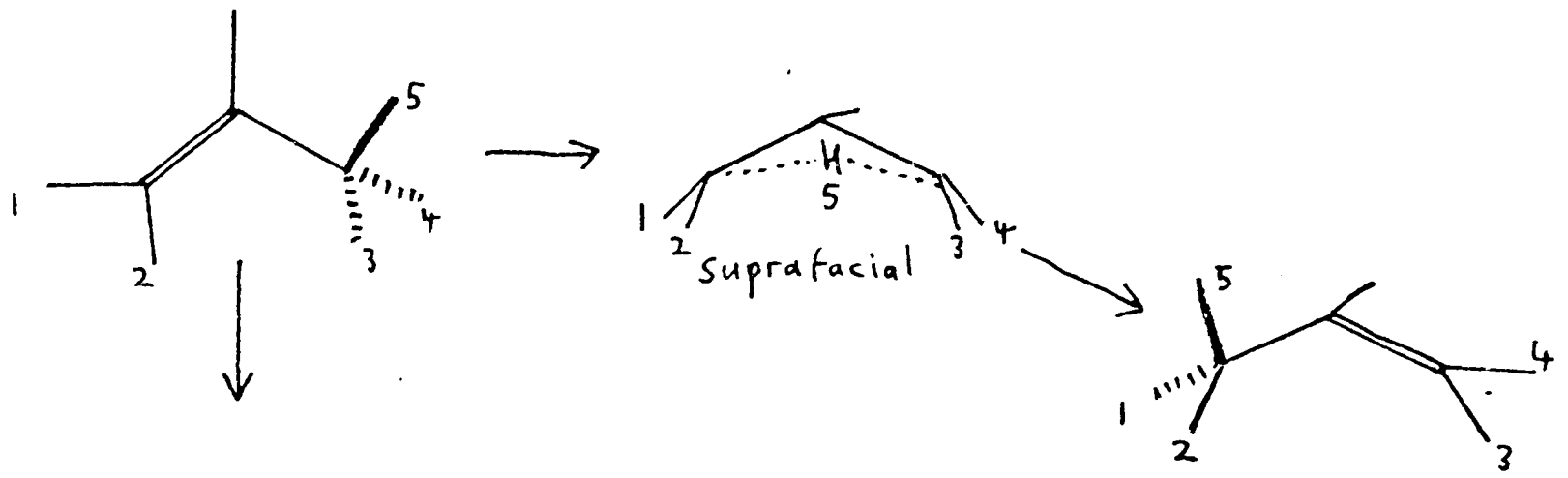
Hückel T.S., 4 electrons
– antiaromatic.

C–H 1.194 Å, C–C 1.31 Å.
C·····C 2.12 Å; All angles 120°.

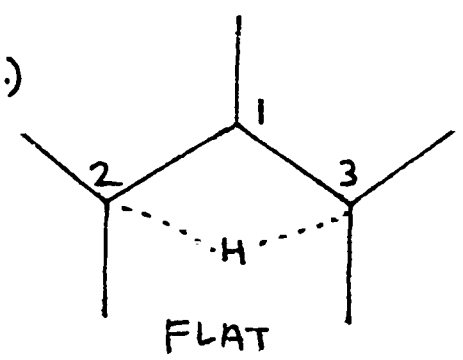
Orbital Number	Type	e^{SCF}_{MINDO}	Symmetry σ_v	Symmetry C_2
10	HOMO π	−0.368	S	A
11	(HOMO−1) σ	−0.355	A	
12	HOMO σ	−0.286	S	
13	LUMO σ*	0.033	A	
14	(LUMO+1) σ*	0.046	A	
15	LUMO π*	0.067	A	S

∴ C_2

Figure 3.24 Details of MINDO MOs For A Model Related to The Dimerisation of Ethylene.



(a.)



FLAT

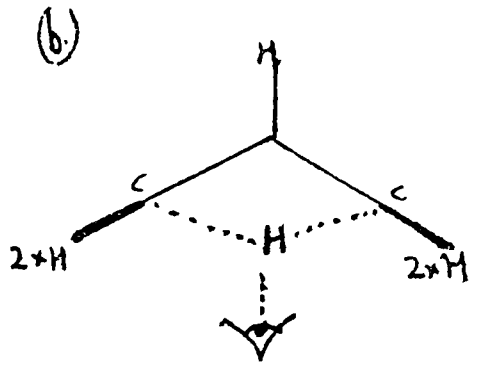
C–H's 1·21 Å
C–C 1·45 Å
H·····C_2 1·45 Å
(and C_3)

All angles 120° or 60°.

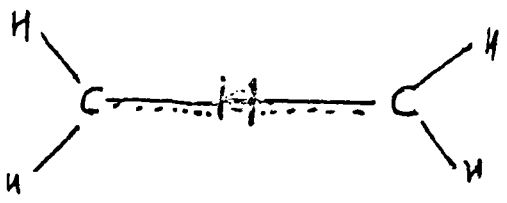
Orbital Number	Type	$e^{S.C.F.}_{MINDO}$	Symmetry σ_v	Symmetry C_2
8	HOMO σ	−0·399	A	
9	HOMO π	−0·285	A	S
10	LUMO σ*	0·020	S	
11	LUMO π*	0·033	S	A

$\therefore C_2$

(b.)



≡ ROTATED



(All bond angles and bond lengths as in (a.), except H·····C_2 = 1·26 Å (αC_3))

Orbital Number	Type	$e^{S.C.F.}_{MINDO}$	Symmetry σ_v	Symmetry C_2
6	HOMO π	−0·462	A	S
7	(HOMO−2) σ	−0·457	A	
8	(HOMO−1) σ	−0·413	S	
9	HOMO σ	−0·255	A	
10	LUMO π*	−0·042	S	A
11	LUMO σ*	−0·033	S	

$\therefore C_2$

Figure 3.25. Details of Models For The 1,3-Sigmatropic Shift in Propene.

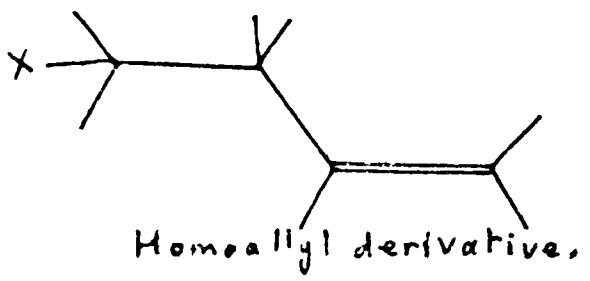
The 'flat' model is shown in Figure 3.25(a). The geometry is the same as that of the allyl type framework in the backbone rearrangement. Again the position of the migrating hydrogen was allowed to vary, but this in no way affected the results. Consideration of the orbital symmetries shown in the diagram once more leads to the correct prediction that the antarafacial transition state is preferred (C_2 distortion).

On rotating the terminal CH_2 groups by 90^o we obtain the rotated version of our model. Orbital symmetry analysis of the HOMO and LUMO orbitals gives the same result as the analysis of the flat model, namely the preference for an antarafacial migration.

It can therefore be said that the HOMO-LUMO treatment outlined previously can be broadly applied for the prediction of conformational preference in pericyclic and acyclic reactions alike. The detailed systems that were studied also showed that HOMO-LUMO interactions alone can account for the stabilisation of the preferred species.

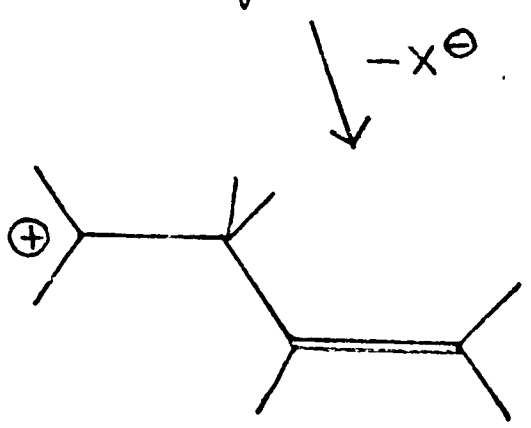
10. The Interconversion of Homoallyl (1.), Cyclopropylcarbinyl (2.) and Cyclobutyl (3.) Cations.

It now appears that the simple Hückel theory is inappropriate for explaining the differences between alternative conformations in transition states/intermediates, in the light of more rigorous calculations. However the previous work involved studies in which the same reaction could occur via two or more T.S.s. Another use of the theory is possible, namely in predicting which of several isomeric species (leading to different products) is the most stable. As an

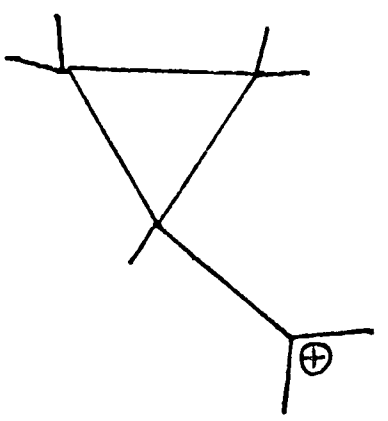


Homoallyl derivative.

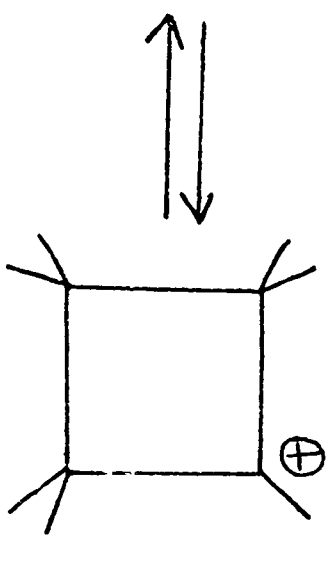
or Cyclopropylcarbinyl / Cyclobutyl derivatives.



(1.) Homoallyl cation.



(2.) Cyclopropylcarbinyl cation.



(3.) Cyclobutyl cation.

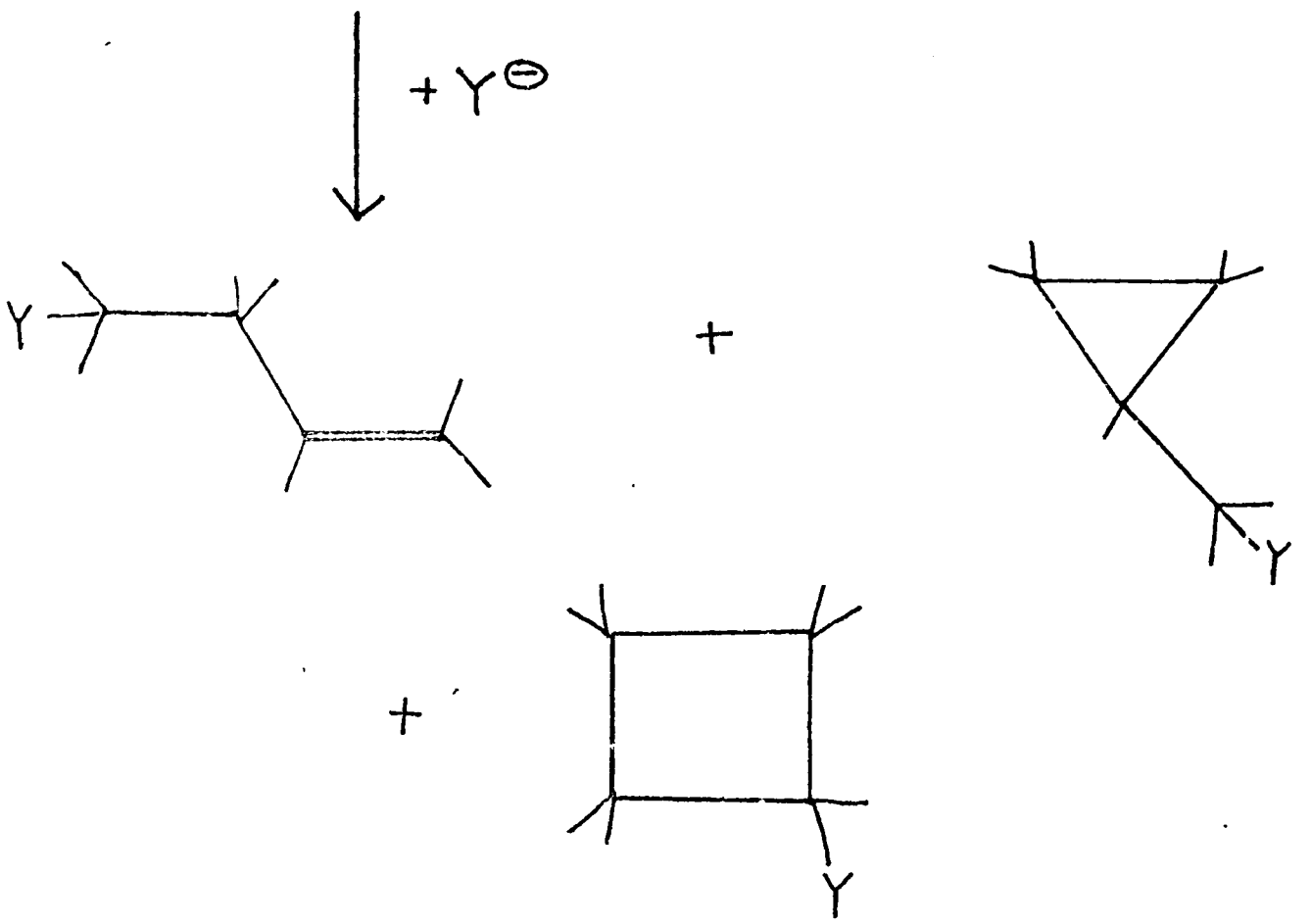
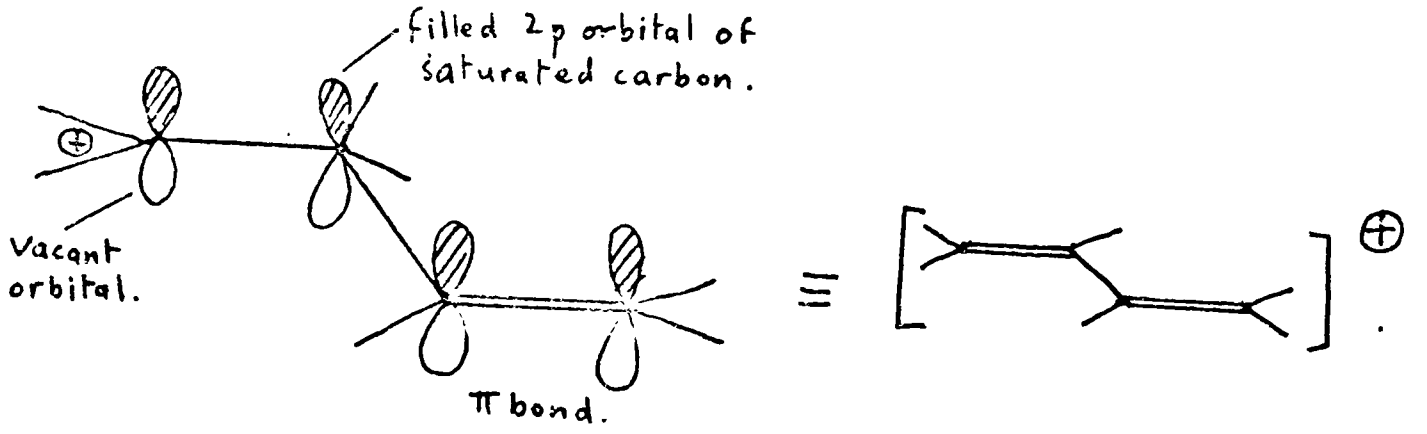


Figure 3.26 Interconversions of C_4 Carbonium Ions.

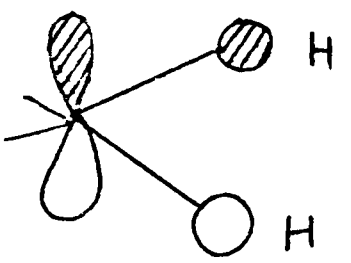
example we may consider the three ions shown in Figure 3.26. They were first postulated by Roberts (1951), as being involved in the solvolyis of their respective derivatives (diazonium, halide, p -tolyl sulphonate etc.), in solvents of low nucleophilicity. The evidence was that all three possible products were observed in roughly the same proportions no matter which of the starting materials was chosen. For a comprehensive account of the work in this field, the excellent review of Wiberg et al. (1972) is recommended. The carbocations themselves have more recently been observed by Olah et al. (1972). However, as yet, there is no experimental information relating to the energy differences between the three ions.

In order to treat this system by the simple Hückel theory, we have to decide the numbers of atoms and electrons involved. If we ignore the saturated carbon, we have a 3-atom, 2-electron example and little further can usefully be deduced about the species. We must therefore investigate the role of this 'non-participating' atom/group, in order to derive any further information. (In the light of our study on the reaction of hydroxide ion with ethylene oxide, introduction of the CH_2 group would appear to be imperative). Now, we can include the CH_2 in two ways. Either we treat the carbon alone and say that only one of its 2p orbitals, containing ~1 electron, will interact with the rest of the 'π' system and hence we now have a 4-atom, 3-electon linear system, butadiene radical cation being its analogue (see Figure 3.27(a.)). Alternatively we may treat the CH_2 in toto. The only filled orbital of the CH_2 group that can interact with the π system is shown in Figure 3.27 (b). We therefore, have a branched 5-atom, 4-electron system. The Hückel π orbitals have been calculated for both these systems by Heilbronner and

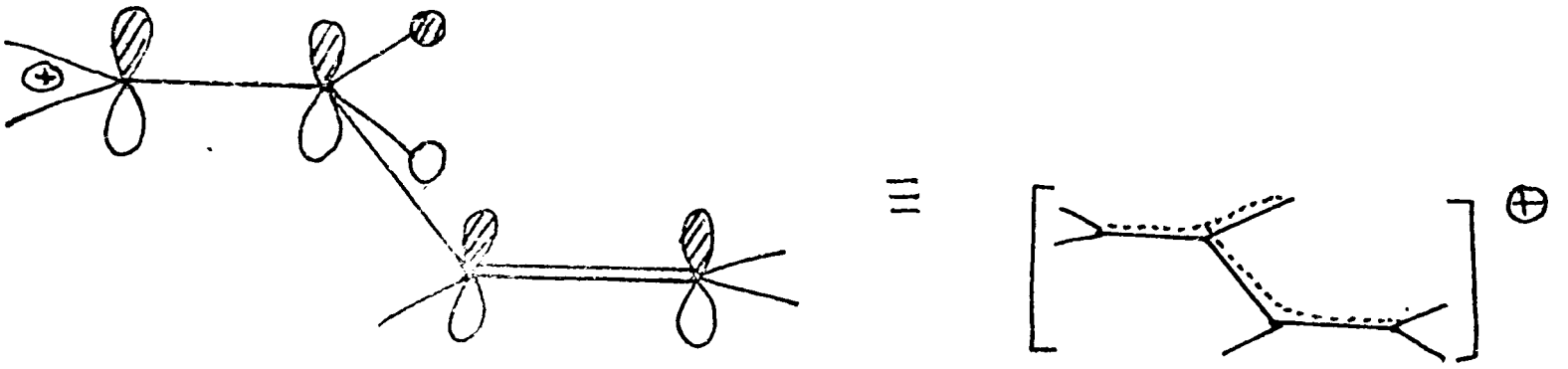
(a.)



(b.)



Filled $-CH_2$ orbital, antisymmetric with respect to the molecular plane.



(c.) Bond orders

	(a.)	(b.)
1,3	0.22	0.0
1,4	-0.09	-0.27

Figure 3.27 Simple Hückel Models For C_4 Carbonium Ions.

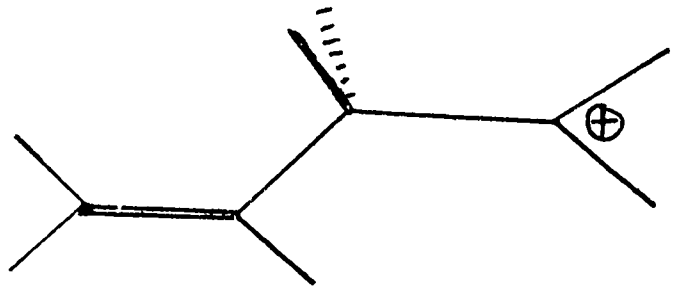
Straub (1966) and the resulting bond order factors are given in the Figure. The cyclopropyl carbinyl cation is predicted to be more stable than the cyclobutyl cation, with the homoallyl cation probably intermediate in energy. (N.B. the last prediction is less certain as we have not taken into account σ bond effects, which may strongly differ between species which possess a ring and those that do not).

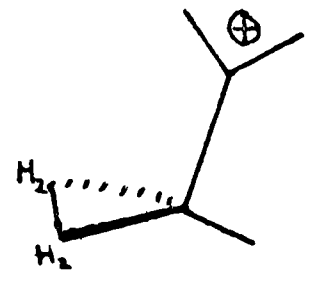
Hehre (1972,1974) has performed extensive GAUSSIAN 70 calculations on the potential surfaces of the three ions and the relative energies which he found are given in Table 3.22. The variation in the cyclobutyl energy is introduced in order to allow for the known deviations from experimental energies found by GAUSSIAN 70 in related neutral hydrocarbons.

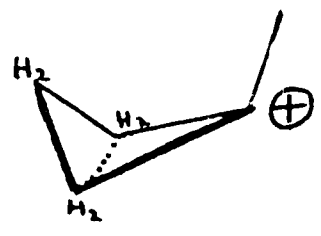
Preliminary OPTMO calculations were carried out on the ions. However S.C.F. convergence difficulties were encountered. Also it was not considered worthwhile pursuing this investigation with MINDO/2, which is known to underestimate strain energies in small rings (the underestimation also varies from ring to ring). However the accurate prediction of the simple Hückel theory, that the cyclopropylcarbinyl cation is the most stable, which is confirmed by Olah and Hehre's work, deserves further investigation. It is likely that MINDO/3 calculations would overcome these difficulties.

11. Final Remarks.

In this section several points, related to many of the previous studies, will be discussed. Then an attempt will be made to place the conclusions of this work in the context of previously described models for organic reactions (see Chapter 1). This will help to clarify the implications and relevance of our results.







Hehre (1972, 1974) – relative energies (kcal/mole)	20.0	0.0	9.4 (± 4.0)
Hückel factors			
(a.) 4 atom, 3 electron	0.0	0.22	−0.09
(b.) 5 atom, 4 electron	0.0	0.0	−0.27

(Geometries are the optimised results of Hehre's calculations).

Table 3.22 Relative Stabilities of The Three C_4 Carbonium Ions.

Firstly, we may ask what is the relationship of calculations on isolated molecules to the actual conditions of a chemical system, in which there is a large number of reacting molecules, usually in the presence of an even greater number of solvent species? From the point of view of the theoretical chemist, there are two ways in which this question can be answered.

On the one hand, we may say that the differences in which we are interested, that is conformational effects in what are otherwise identical species, will be virtually unchanged by solvation energies, which might be expected to affect the various conformations equally. Thus although reactants, products and intermediates will be affected unequally (possibly leading to a change in their nature), within each of these three groups the relative energies will be maintained. (For example, in most of our studies we were comparing species more stable than the 'reactants and products', i.e. intermediates. However solvation effects make these species transition states in the solution reactions). Thus our inferences from the calculations are still applicable to the actual situation occurring during reaction. However this argument is a rather defensive one and it restricts the range of comparative theoretical studies to species of similar type.

A more positive case for theoretical investigations of the type that have been described is as follows. Organic reactions are invariably depicted as involving the interaction of isolated molecules and solvation effects etc. are introduced as secondary factors, if at all. The experimental data is therefore assumed to indicate the properties of these single molecules. However such effects as solvation can be decisive and in certain systems produce results in direct opposition to the trends in the isolated molecules (see below). Therefore only when the reactions of the isolated molecules have been studied (and

this can usually only be achieved by means of calculations), is it possible to discover the precise origin of any experimentally-observed effects.

As an example of the above, we may consider the work of Richards and Dean (1975). It is generally proposed that methyl groups are electron donors, relative to hydrogen. Richards and Dean performed GAUSSIAN 70 calculations on the ammonium ion and methyl-substituted homologues. The electronic charge in a fixed sphere around the nitrogen atom (radius .7Å, one covalent radius) was found by integrating the derived wave function. The calculated charges are as follows,

Species.	$NH_4^{\oplus}$	$CH_3.NH_3^{\oplus}$	$(CH_3)_2\ NH_2^{\oplus}$
Charge.	5.054	4.774	4.492

Further evidence for this order is obtained from dipole moments, spectroscopic effects etc. The decreasing charge on the nitrogen atom with increasing methyl substitution is in direct opposition to the traditional proposition given above. The authors conclude that solvation and polarisability effects produce the reverse order often found in solution for these species and that the usual explanations, in terms of electron-donating capacity, are in fact the antithesis of the actual situation.

We will now return to a question that has been discussed previously; that is, what determines the size of orbital mixing when a molecular geometry is distorted, and in particular why are HOMO-LUMO, σ/π, interactions the largest in the distortions which we have analysed? The degree of mixing for small distortions, we know to be given by $H'_{iojo}/(e_{io}-e_{jo})$. We have seen for $CH_5^{\oplus}$ that energy gap alone is an insufficient reason for the observed predominance of HOMO-LUMO mixing. We also gave qualitative reasons for the preference for σ-π rather

than σ-σ and π-π electron transfer. However the value of H'_{iojo} for different π-σ mixings was not found to correspond to any simple overlap term. It is possible that $CH_5^{\oplus}$ is in some ways a special case in that only one π orbital is present.

In the examples where there were more π orbitals, the HOMO-LUMO, σ/π, interactions were still the greatest. These borderline orbitals of similar eigenvalue were also seen to possess similar nodal properties and electron distributions with respect to the main atoms involved (e.g. Figures 3.10, 3.12). The increased electron transfers can therefore be rationalised to some extent, bearing in mind that H'_{iojo} is related to overlap of the orbitals ϕ_{io} and ϕ_{jo}. Thus when several main atoms are present, π and σ orbitals with the same pattern of nodes and with large contributions on the same atoms should have a large interaction on perturbing the geometry. Also since orbitals with similar nodal patterns will have similar eigenvalues the energy gap consideration will further favour their interaction.

The reason for the choice of (HOMO-1)σ and (LUMO+1)σ orbitals rather than π orbitals, for the consideration of secondary effects (cf Pericyclic section, Chapter 3) is related to the above conclusion. Since there are in general more σ orbitals than π orbitals, this implies that there is invariably more than one σ orbital with the same nodal patterns, with respect to the main atoms, as the HOMO (or LUMO) π orbital, whereas the reverse is not true. Thus these 'subjacent' and 'superjacent' σ orbitals which have these nodal properties (cf. Figure 3.12) will be of more importance than the corresponding π orbitals in electron transfer.

If the above is qualitatively correct, how can we explain the

results found for $CH_5^{\oplus}$? To do this, one must analyse the term H'_{iojo}. This is the off-diagonal Fock matrix element, between m.o.s ϕ_{io} and ϕ_{jo}, caused by the perturbation, (ϕ_{io} and ϕ_{jo} are orthogonal in the unperturbed system). This matrix element can be broken down,

$$H'_{iojo} = F'_{iojo} = H^{o\prime}_{iojo} + \sum_{Ko \neq jo} \int \phi_{io}(2J_{ko} - K_{ko})\,\phi_{jo}\, d\tau$$

(old m.o.s-new positions) (core matrix part) (electron-electron part)

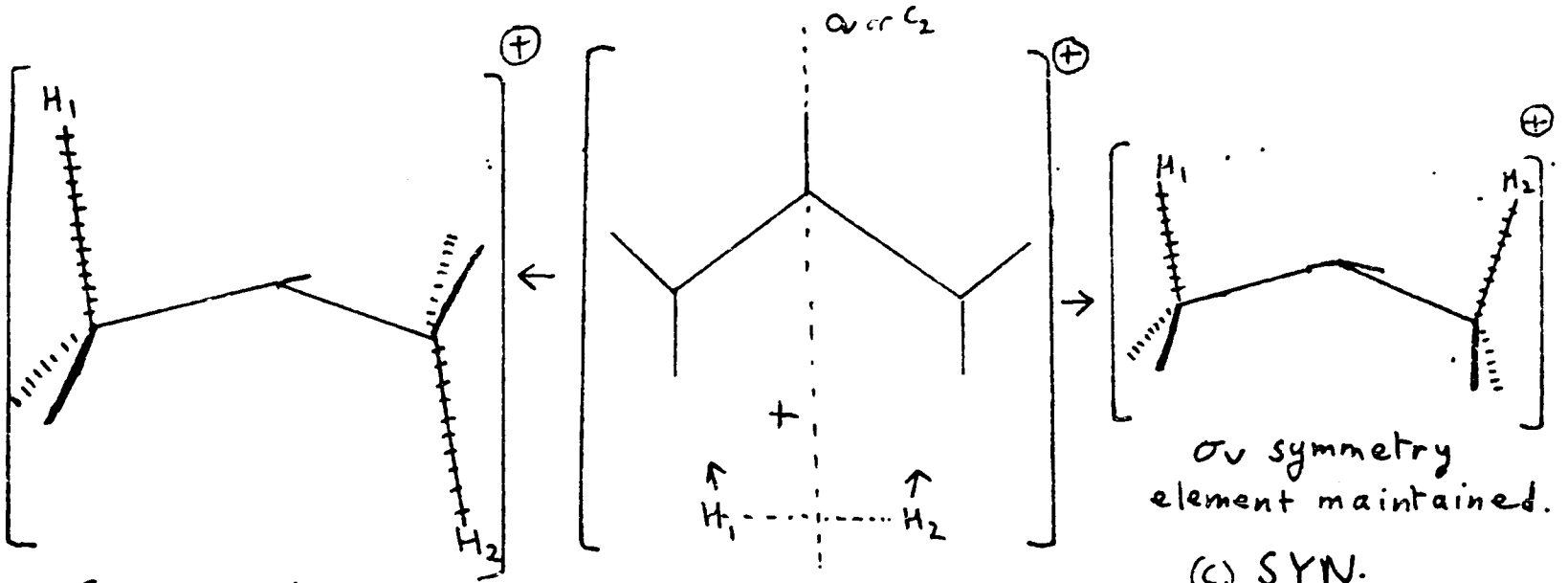
The above analysis in terms of overlap includes only the value of $H^{o\prime}_{iojo}$, the two m.o. part, since the second summation of terms involves the interaction of ϕ_{io} and ϕ_{jo}, together, with all <u>other</u> m.o.s ϕ_{ko}. This latter contribution is not amenable to even qualitative analysis since it is made up of a large number of terms, each of which contains a different set of three m.o.s! We may deduce empirically however that in the distortions to 'flat' $CH_5^{\oplus}$, these three-m.o. terms are of importance in favouring the HOMO-LUMO transfers and it is quite possible that this is also true for the more complex systems studied.

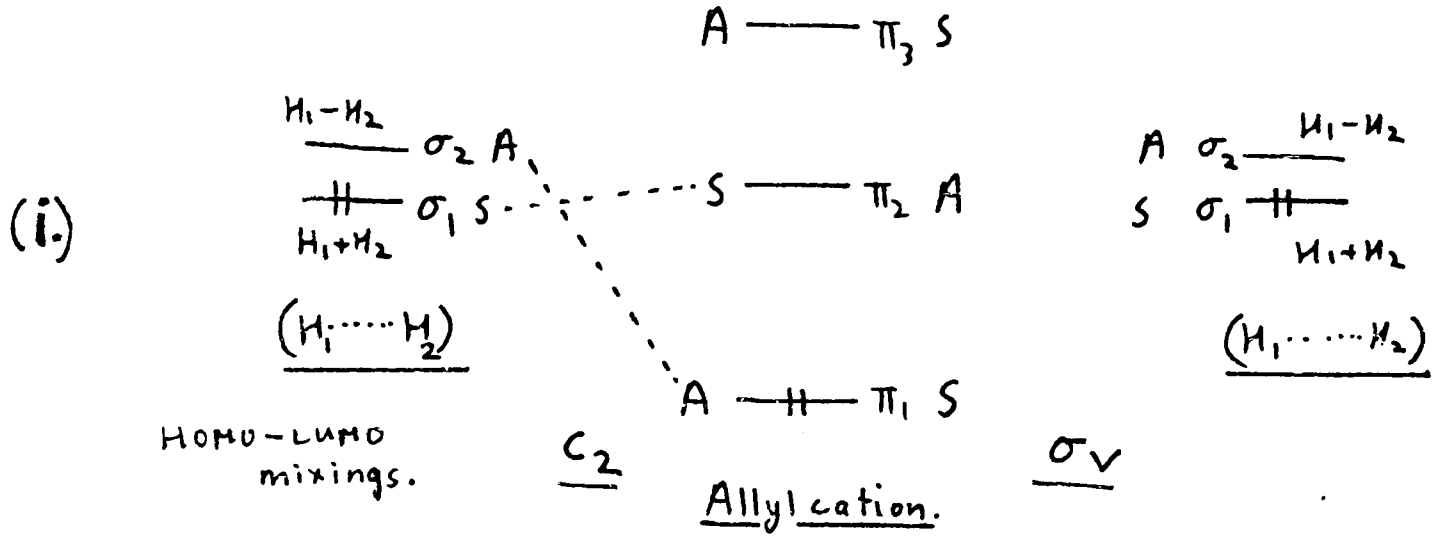
We may therefore conclude that σ-π interactions are greater than σ-σ and π-π interactions because of overlap considerations and that in general σ and π orbitals with similar nodal properties for the main atoms will have large interactions. Whether the latter observed effect is due to overlap factors or 'J and K' factors in not easily established. However we can definitely say that all these factors, together with energy gap considerations, combine to favour the predominance of HOMO $\left\{\begin{matrix}\sigma\\ \pi\end{matrix}\right.$ - LUMO $\left\{\begin{matrix}\pi^*\\ \sigma^*\end{matrix}\right.$ mixings in geometrical perturbations.

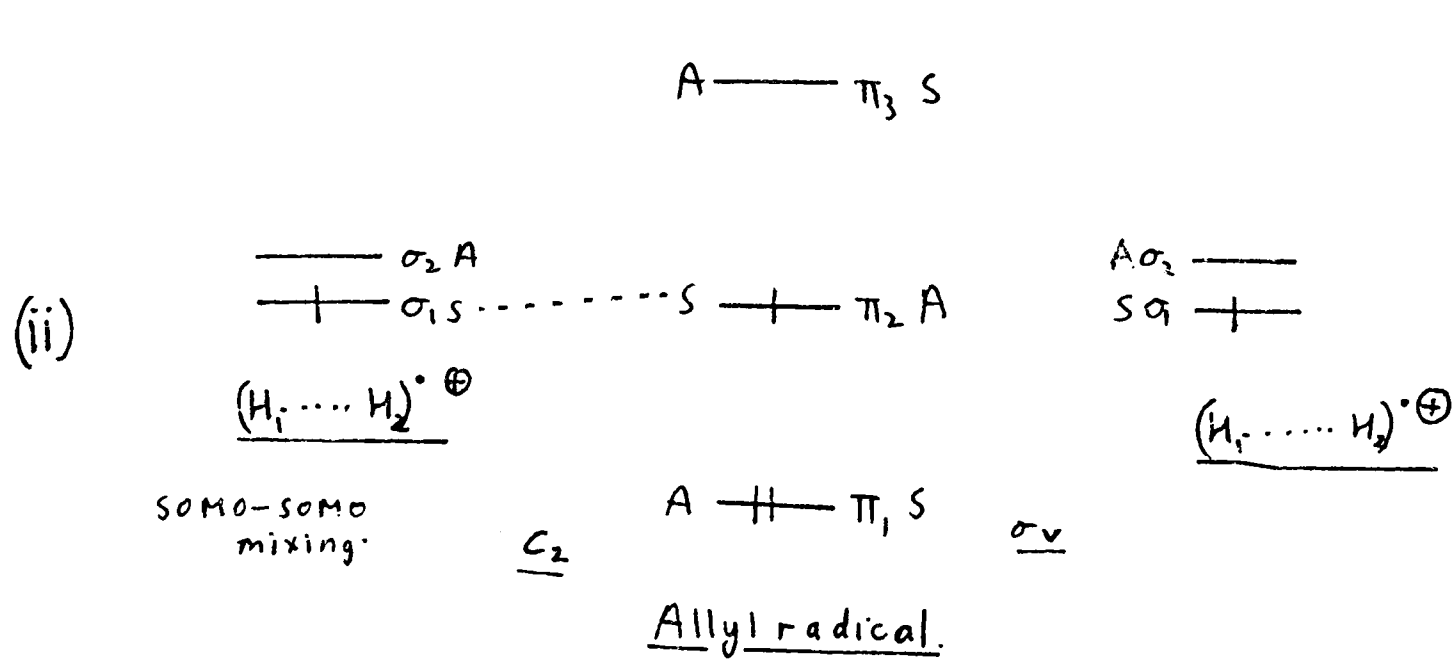
Having established the means for understanding and predicting the conformational preference of a large number of organic reactions, namely by setting up and inspecting the m.o.s of, and/or distorting the geometry of, symmetrical intermediate models, we have something of a problem. This is the fact that it is necessary to perform a calculation on each system in which we are interested, in order to show that our conclusions are still valid for that particular example. In other words, in order to employ our general axioms we must perform calculations involving all the electrons. This is mainly due to the fact that although we can deduce the qualitative nature of the π orbitals in a particular system, the σ orbitals are much too numerous and complex to be so treated.

If we wish to derive a model which can be more easily applied, we must simplify our treatment of the σ framework. We shall proceed to do this, accepting that this <u>is</u> a simplication, and shall discuss afterwards the relationship between our two models. The model we shall develop will also have very close links with the previously described treatments of pericyclic reactions.

The basis of our approach will again be the consideration of an intermediate symmetrical set of 'reactants' which can be converted into either of the two T.S.s/intermediates. Perturbation theory will then be applied to the 'essential' orbitals of the reactants, as distortions towards the intermediates allow them to mix. For example, we studied the attack of a proton on propene as a model for the S_E2' reaction. The two intermediates are shown in Figure 3.28 ((a.) and (c.)). We have also depicted in (b.) a pair of reactants, i.e. an allyl system and a coplanar symmetrical H....H system, which can be converted into the intermediates. In one case the hydrogens would







In both cases, distortion preserving C_2 symmetry is preferred, leading to the anti species.

Figure 3.28 Simple Model For The S_E2' Reaction.

approach and both rise above the plane (→SYN geometry), while in the other case, one would rise above and one would sink below the plane on approach (→ANTI geometry). In the intermediates, the H.....H. bond has been replaced by the C.....H bonds, i.e. the H.....H through space interaction is only present for the initial approach to the intermediates, which is all that shall be of interest.

To analyse this model and the distortions to it, we must consider which orbitals play the major part. Taking into account our previous studies we may presume that the main orbital interactions that occur on moving the hydrogens out of the molecular plane, will be between the σ orbital(s) of the H.....H bond and the π orbital(s) of the allyl system. The energies of these two sets of orbitals are given in the Figure, together with their symmetries with respect to the different symmetry elements maintained during the possible distortions. The bonding combination ($H_1^{1s} + H_2^{1s}$) of hydrogen a.o.s is more stable than the antibonding combination.

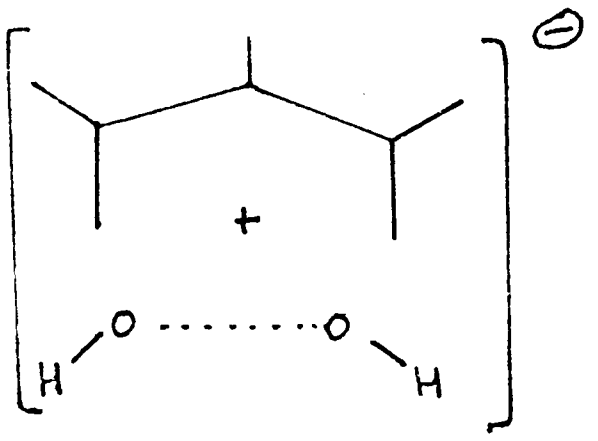
Now we must determine the number and distribution of electrons. Two sets of 'reactants' might seem to be appropriate, i.e. allyl cation and H.....H neutral or allyl radical and H.....H radical cation. Assuming for the moment that the first is more appropriate, the number of π electrons in the allyl system is two and the number of electrons in the H.....H σ bond is two (as shown in the Figure). We observe that in order for HOMO$\left\{\begin{matrix}\sigma\\ \pi\end{matrix}\right\}$ - LUMO$\left\{\begin{matrix}\pi^*\\ \sigma^*\end{matrix}\right\}$ mixing to occur on perturbing the system we must preserve the C_2 symmetry element. Thus the distortion leading to the anti geometry is preferred. (N.B. We might suggest that when allyl cation and H.....H is the model, the major transfer will be from H.....H to the allyl species, i.e. HOMOσ - LUMOπ^*, since this smoothes out the charge distribution in the overall system).

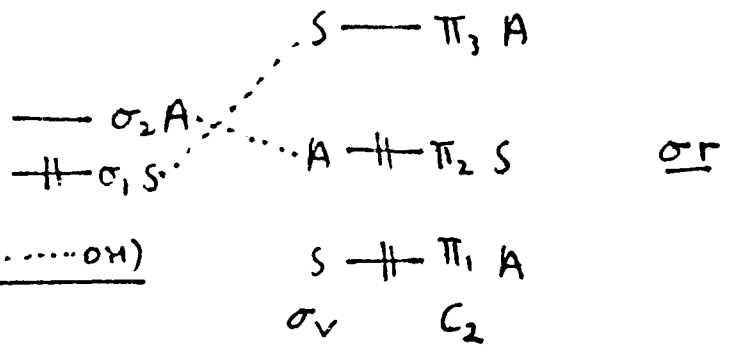
If we choose allyl radical and H.....H radical cation as our model, we then have a singly occupied m.o. (SOMO) in each set (see Figure). The mixing of greatest importance in such a system is between these two SOMOs. We observe again that these orbitals can only mix if the C_2 element is preserved during the distortion. Thus both models lead to the same correct prediction (NB. Here we might expect the major transfer to be from the allyl radical to the H....H radical cation, because this π-σ^* transfer leads to a more even electron distribution. In other words, after an anti distortion, the true situation is probably in between these two models).

For the S_N2', we have merely replaced the H's by OH's and the overall sign has changed from +1 to -1. Of course the OH's contribute other electrons to the π and σ framework, but we will assume that it is only the σ bonds being broken and formed and the allyl π system that are of decisive importance, for the initial distortions (see Figure 3.29(a)). We now have two more electrons <u>in toto</u> and whichever way we distribute them, we find that HOMO-LUMO or SOMO-SOMO, σ/π, considerations lead to the correct prediction that a syn geometry is preferred. Likewise we can draw similar diagrams for our elimination model, S_E2, S_N2 and backbone reactions (Figure 3.29 (b),(c),(d),(e)). In all cases, the predictions agree with the experimental data and our previous calculations.

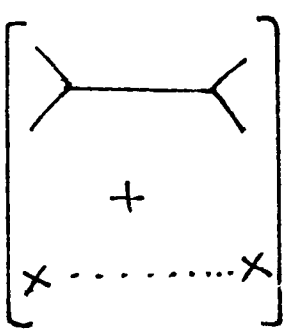
In the general case, there will be a bonding (S) and antibonding (A) combination for the incoming groups, of which the S combination will be the more stable. There will also be a number of π orbitals, the symmetries of which alternate with energy, the most stable being symmetric with respect to σ_v and antisymmetric with respect to C_2.

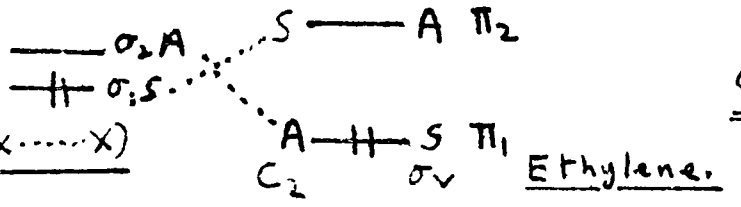
(a) S_N2'



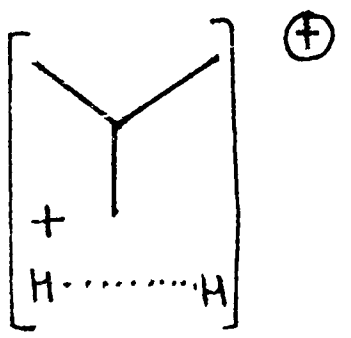


(b) 1,2 Elimination.





(c) S_E2



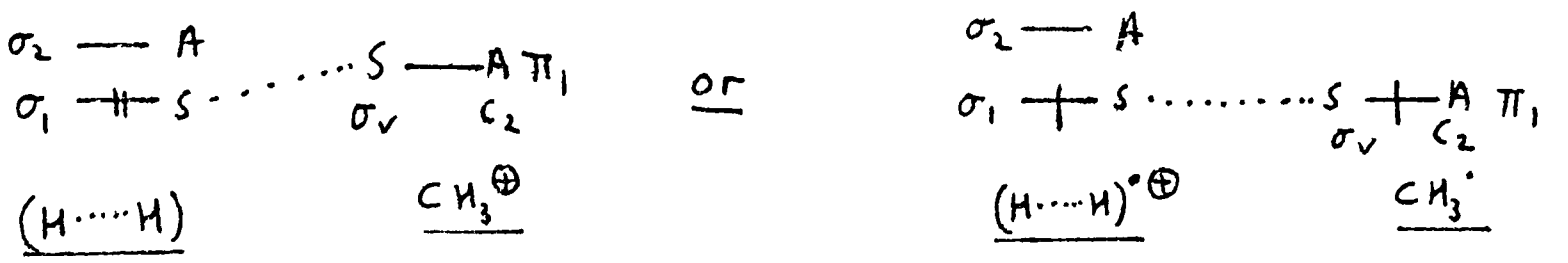
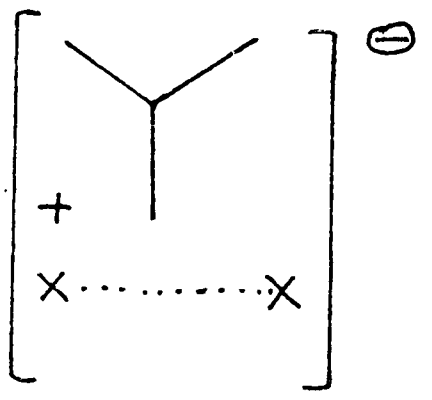
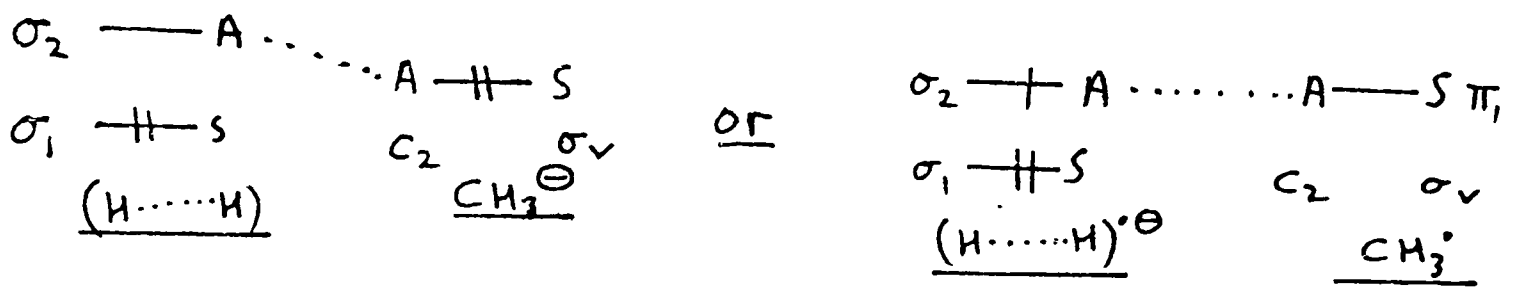


Figure 3.29(i) Simple Models of Acyclic Reactions.

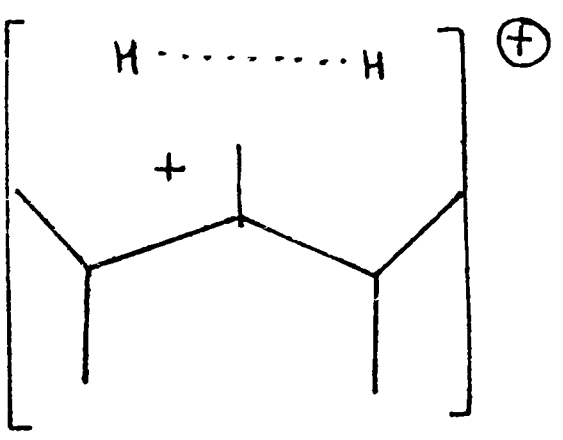
(d) S_N2

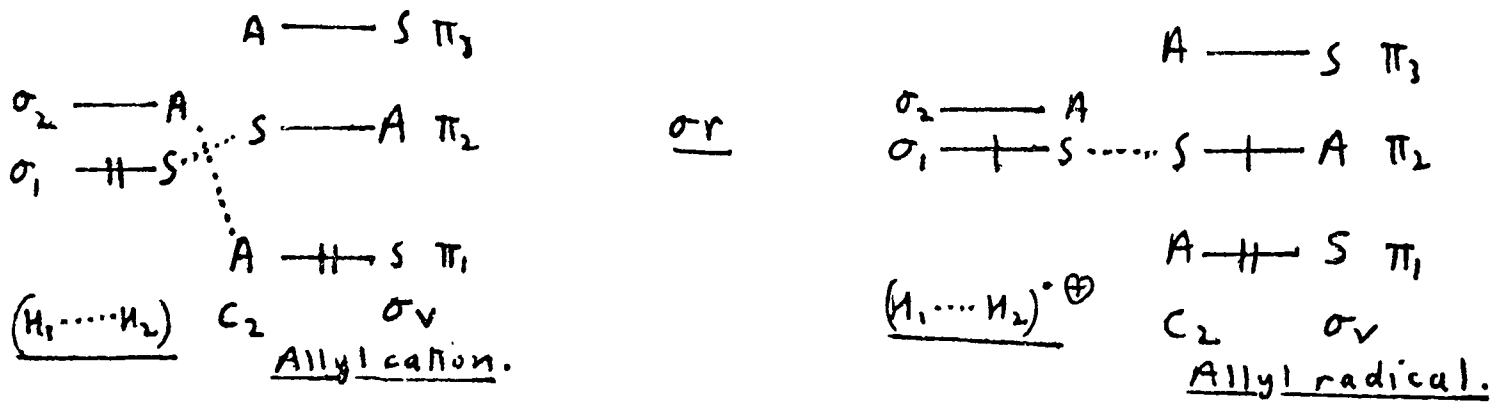




$C_2 \equiv$ anti

(e) Backbone Migration.





$C_2 \equiv$ anti

(N.B. The orbital diagrams are identical with those for the S_E2' model – Figure 3.28.)

Figure 3.29(ii) Simple Models of Acyclic Reactions.

One may deduce mathematically, or by inspection of the examples given, that the syn distortion is favoured when the total number of electrons in the π and σ 'essential' orbitals can be expressed as $4n+2$ and the anti distortion is favoured when the total number can be expressed as $4n$, where n is a whole number, possibly zero. Table 3.23 shows that this is so for the reactions that have been studied.

This conclusion for acyclic reactions is complementary to that derived in the Hückel/Möbius treatment of pericyclic reactions (see Chapter 1). This relation is due to the fact that in our present simple model, we introduce a bond between the atoms/groups that become the ends of the acyclic 'chain' in the intermediates, in order to differentiate in terms of energy between the two σ combinations. Thus as interactions are brought about (between the σ and π m.o.s), by the distortions, we have a form of cyclic array for which similar considerations apply as in the pericyclic analysis. In fact the whole present approach is reminiscent of Woodward and Hoffmann's (1970) observation that all T.S.s in pericyclic reactions can be considered to be formed by cycloaddition of two 'reactants'.

However there is a major difference between the pericyclic and present acyclic treatments. In the pericyclic study the cyclic arrays are found in the T.S.s; whereas cyclic arrays are only invoked for the initial stages of reaction and our simple model is a perturbational approach. We do not suggest that there is a cyclic 'aromatic' array in the preferred T.S. that is responsible for conformational preference in acyclic reactions and our calculations have shown this not to be so.* This is in contrast to the originally proposed simple Hückel theory, where an explanation of precisely this nature was used, i.e. the through space interaction between the incoming and leaving groups differentiates

Reaction.	Total Number of Electrons.	Reaction Preference.
S_E2	2	SYN
S_N2	4	ANTI
E 2	4	TRANS (ANTI)
S_E2'	4	ANTI
BACKBONE	4	ANTI
S_N2'	6	SYN
In general:	4 N	ANTI
	4 N+2	SYN.

Table 3.23 Reaction Preference As A Function of The Total Number of 'Essential' σ and π Electrons.

between the two T.S.s/intermediates.

We may continue this train of thought, in order to link up our present simple theory with the more sophisticated treatment, involving all electrons, derived from the calculations. We know from our results and energy breakdowns that in almost all cases, stabilisation of the allowed intermediate is due to stabilisation of the σ framework in the π hydrocarbon base. This is not treated by the simple model. But as we know, when the X....X moiety is brought up to the rest of molecule, the two σ frameworks mix and in the intermediates themselves the two groups X interact both by through space and <u>through bond</u> interactions (for the S_N2' and S_E2' intermediates, through bond interactions are probably of greater magnitude). The latter interactions involve the whole σ framework and hence all the σ a.o.s are mixed in the resulting m.o.s. The all important borderline σ m.o.s therefore contain contributions from many a.o.s of the σ basis set, as we have seen. It is this mixing which produces the observed stabilisations. Thus the simple model is a perturbation treatment inspired more by the ideas of Fukui than the ideas of Dewar and Zimmerman.

In fact Fukui has used the formalisms of HOMO-LUMO σ/π mixing (1969a) and 'cyclic' acyclic systems (1967) - his own words - to describe reaction preferences of the type considered. However as with many of his acyclic studies (see chapter 1), he only considers one of the reactants, namely the π hydrocarbon part of our simple model. This results in the necessity for a rather arbitrary and often bizarre method for determining the number of electrons involved and the interactions that are of importance. They will not be discussed further here, but their value in providing a basic framework for the previous discussions is nevertheless significant.

In conclusion, we may say that the preceding remarks provide a general thesis which can explain and predict the stereospecificity of a large number of acyclic organic reactions as well as demonstrating the links between stereospecificity in both pericyclic and acyclic reactions.

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Appendix 1.

Molecular Orbital programs.

1. The ATMOL/2 Ab Initio Program.

This set of programs, due to Hillier and Saunders (1970) uses basis functions of the gaussian type, but not of the general form given in Chapter 2. The major difference is that the angular part of the function is given in terms of the three Cartesian coordinates rather than the spherical harmonics,

$$N.e^{-\zeta r^2}.\ x^i\ y^j\ z^k$$

where N is a normalising factor and the coordinates have their origin at the function centre. Integrals are only used if greater than 10^{-10}, the wave functions obtained are such that the elements of the density matrix are correct to within 10^{-5}, and the energy to within 10^{-10}.

In the open-shell calculations, the diagonal blocks of the Fock matrix were all constructed using the following Hamiltonian,

$$H = F + 2J\ (R_1) - K(R_1) + J(R_2)$$

Where F is the matrix representative of the 1-electron operator, J and K are the coulomb and exchange matrices respectively for a given density matrix (R), the matrices being R_1 for the closed - shell electrons and R_2 for the open-shell electrons. It has been found that this choice is the optimum for obtaining convergence.

2. The GAUSSIAN 70 Ab Initio Program.

As in the ATMOL program, gaussian type basis functions are employed. In the calculations performed, the STO-3G basis set was used. This means that each STO basis function is replaced by a least square fitted set of 3 gaussian type orbitals. However an additional simplification is added, in order to strongly decrease the integral evaluation time.

This entails setting the exponents, ζ, for the 2s and 2p functions, to the same values. This apparently has little effect on the results obtained.

Mention is also made in this work of the STO 4-31G basis set, used by Pople and coworkers. Here the inner core STO functions are replaced by a set of 4 least squares fitted gaussians and the valence STOs are replaced by a split set of three inner and a fourth outer gaussian functions. In other words the valence orbitals have two variable elements in their constituents, allowing greater flexibility in the calculations, but also significantly increasing the integral evaluation time. Several basis sets are available with the GAUSSIAN 70 package, but only the STO-3G set was used, because of the prohibitive amount of computer time required for the more complex basis sets.

A geometry optimisation package was also available and was occasionally employed. This allowed one to vary any number of molecular parameters (bond angles and bond lengths) either simultaneously, by fixed amounts, or independently. Three energy points were calculated with defined values for the parameter(s) being varied. The three points were fitted to a parabola and the minimum energy point was found, together with the corresponding value(s) for the parameter(s). When all required parameters had been varied, a final calculations was performed, using all the optimised values obtained.

3. OPTMO and its Modifications.

The details of the MINDO/2 program have been given in Chapter 2. The modified input for OPTMO will be briefly described, together with the changes introduced into the production of the output.

Besides standard input variables (i.e. time limit, title, Cartesian coordinates (in a.u.) S.C.F. parameters, etc.), the following parameters are present.

(i) A parameter which specifies whether a single calculation is to be performed or whether geometry optimisation is required. If the latter, a final energy gradient limit is given (see Chapter 3).

(2) A matrix of numbers (0 or 1), which specify the Cartesian coordinates that can vary (1) and which are fixed (0), when optimisation is performed. This is used when reaction pathways are being studied, or in order to maintain certain symmetry elements. In the former case, the step size required for the reaction coordinate changes is given, together with a final value for this distance, which when reached causes the calculations to terminate.

When the eigenfunctions have been found, the original program merely produced the eigenvectors and their eigenvalues, and the density matrix. The following functions are now also calculated and their uses and relevance have been described elsewhere.

(1) The orbital energy breakdown matrix, derived from the Fock matrix and the density matrix.

(2) The total energy breakdown matrix, derived from the Fock, Core Hamiltonian, density and nuclear repulsion matrices.

(3) The bond order matrix, derived from the density and overlap matrices.

(4) The atom-atom bond order matrices, a condensed version of (3).

(5) The 1-electron core orbital energies, derived from the eigenvectors and the Core Hamiltonian matrix.

Other minor parameters and changes were also introduced, but they do not warrant mention here.

Appendix 2

Optimised Geometries of Various Species.

The XY,XZ and ZY projections are given for the OPTMO-derived geometries of the following species (excluding 6.),

1. $CH_5^{\oplus}$ - C_s symmetry.
2. $CH_5^{\oplus}$ - D_{3h} symmetry.
3. $CH_5^{\oplus}$ - C_{4v} symmetry.
4. $CH_5^{\ominus}$ - D_{3h} symmetry.
5. Allyl alcohol.

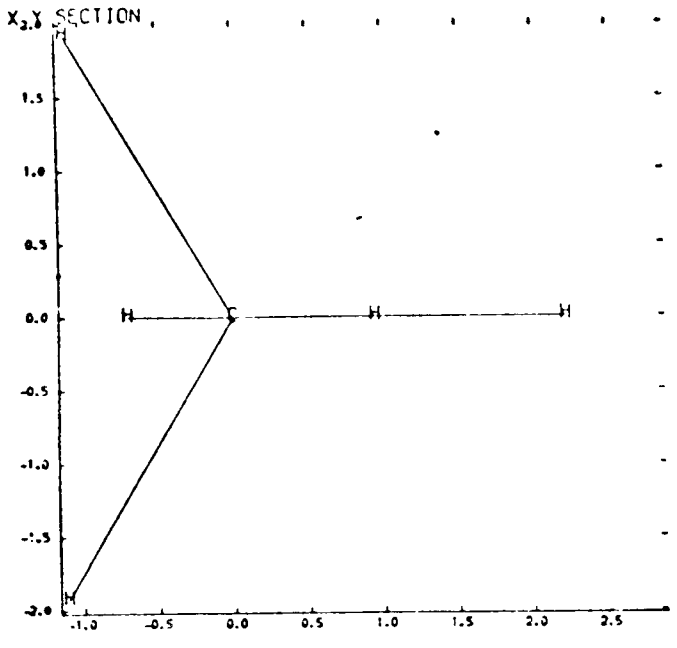
*6. S_N2'; ab initio results for allyl alcohol plus hydroxide ion etc..

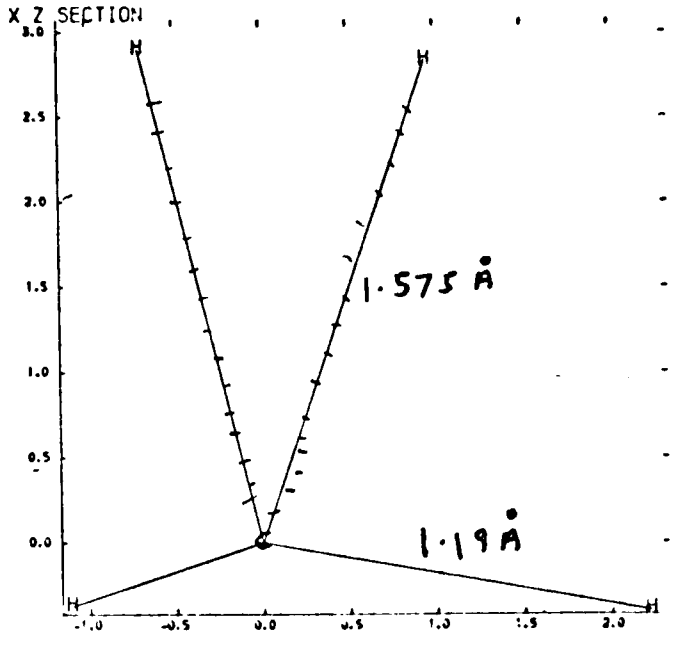
7. S_N2' - syn intermediate.
8. S_N2' - anti intermediate.
9. S_E2' - syn intermediate.
10. S_E2' - anti intermediate.
11. Propene.
12. $C_3H_7^{\oplus}$ - eclipsed 2-propyl cation.
13. Ethylene oxide plus hydroxide ion - 'rear' T.S.
14. Ethylene oxide plus hydroxide ion - 'front' T.S.
15. Ethylene oxide.

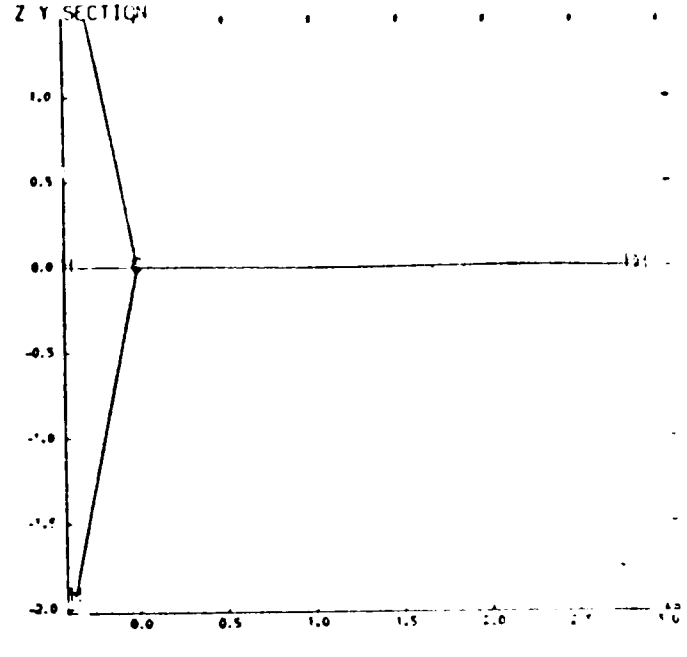
(*Here the details are given for the GAUSSIAN 70 calculations on these species.)

The scales are in a.u., and all bond lengths are given in Å, to the nearest .005 Å.

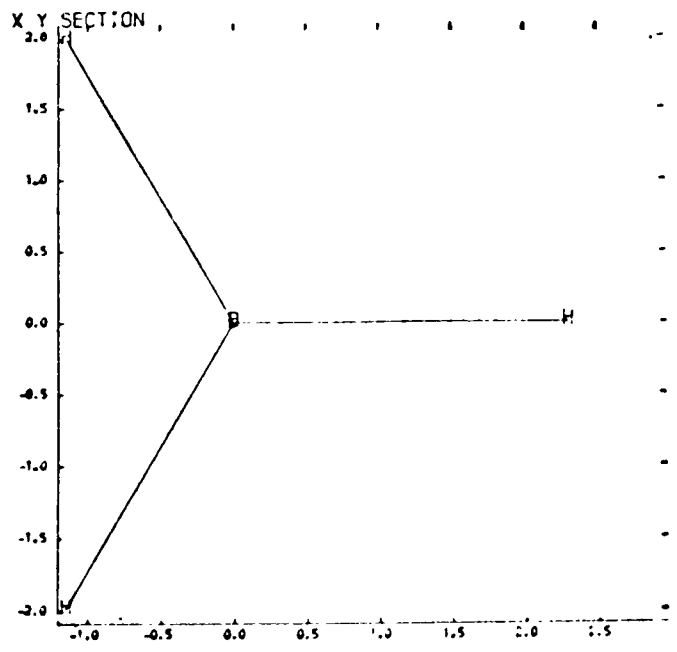
1. $CH_5^{\oplus}$ – C_s symmetry.

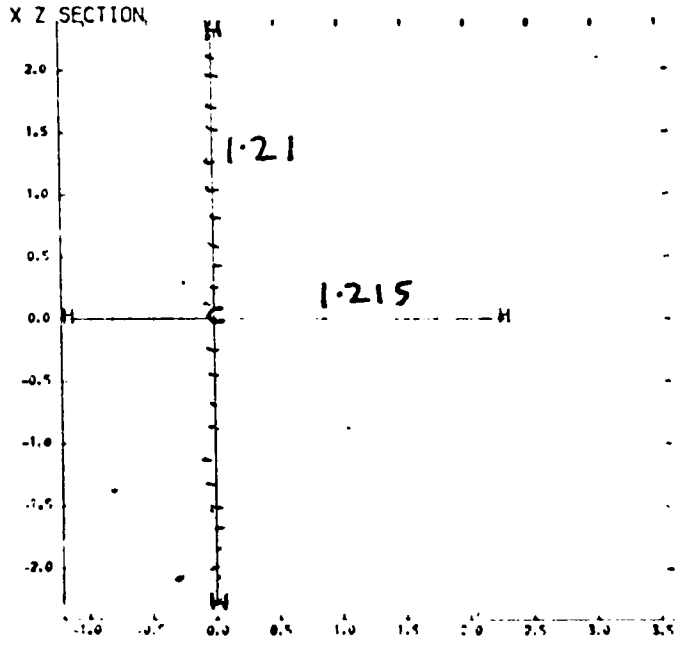


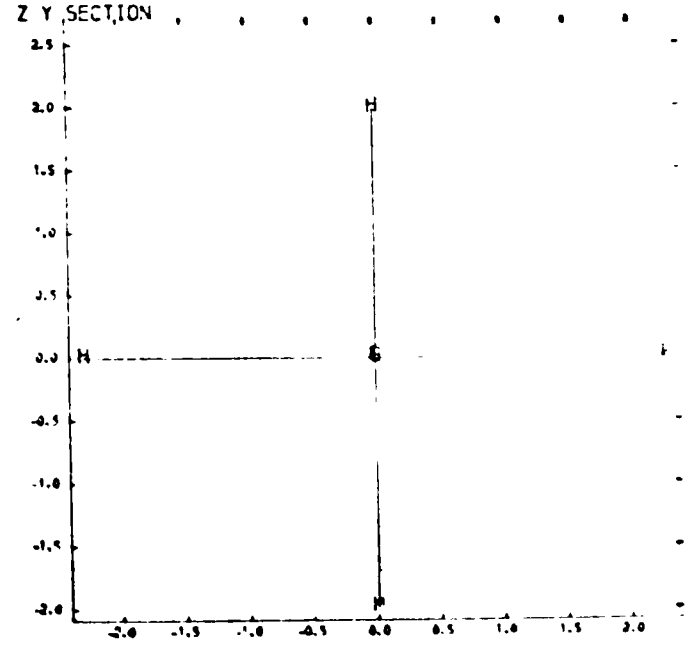




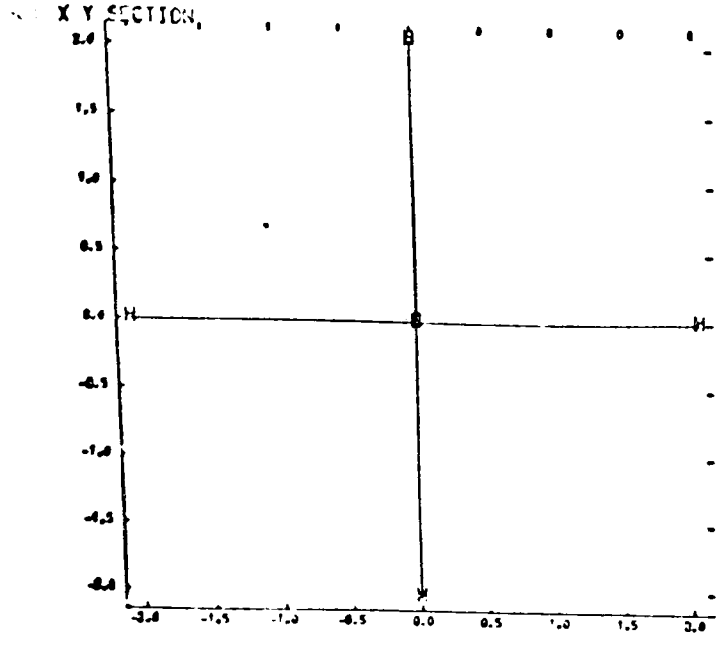
2. $CH_5^{\oplus}$ – D_{3h} symmetry.

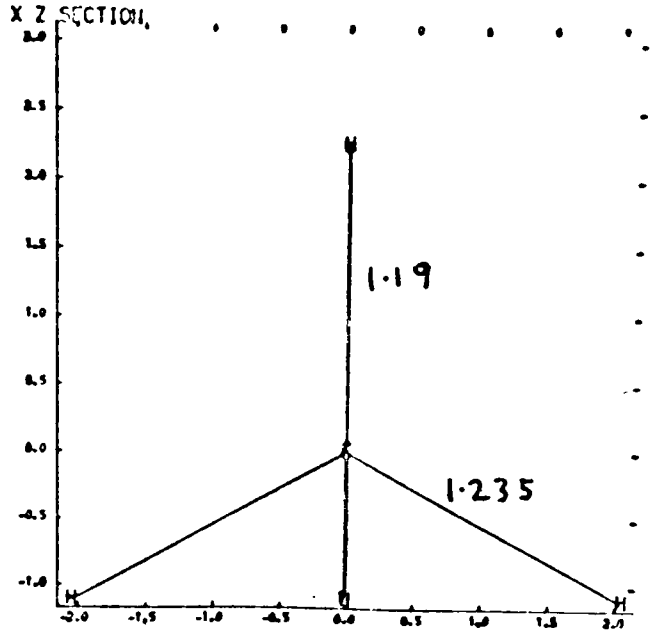


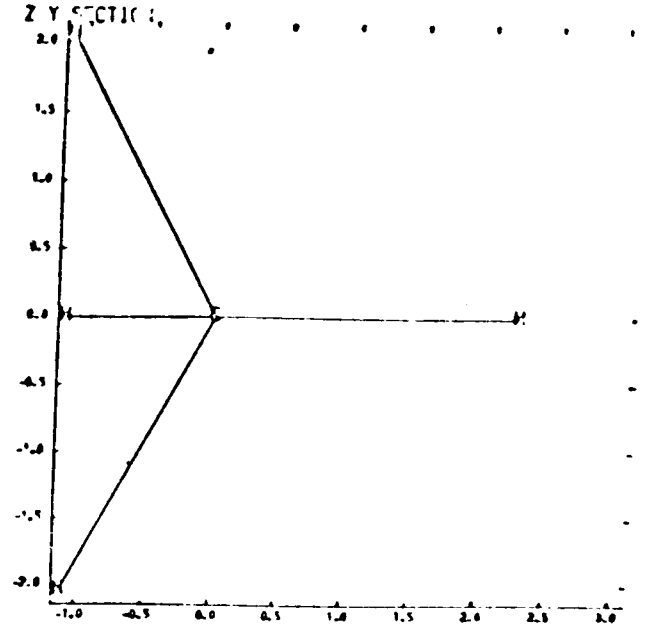




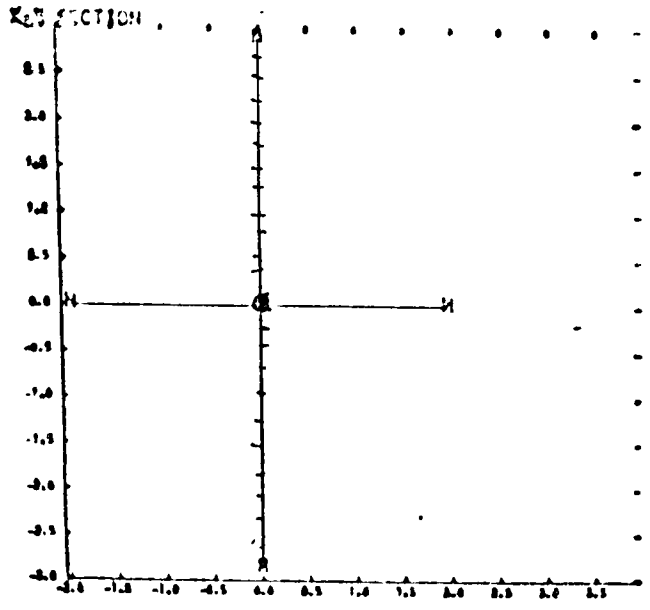
3. $CH_5^{\oplus}$ — C_{4v} symmetry.

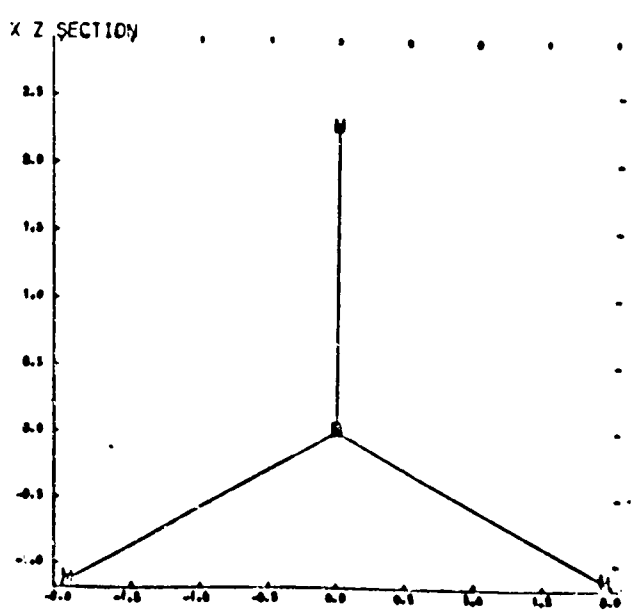


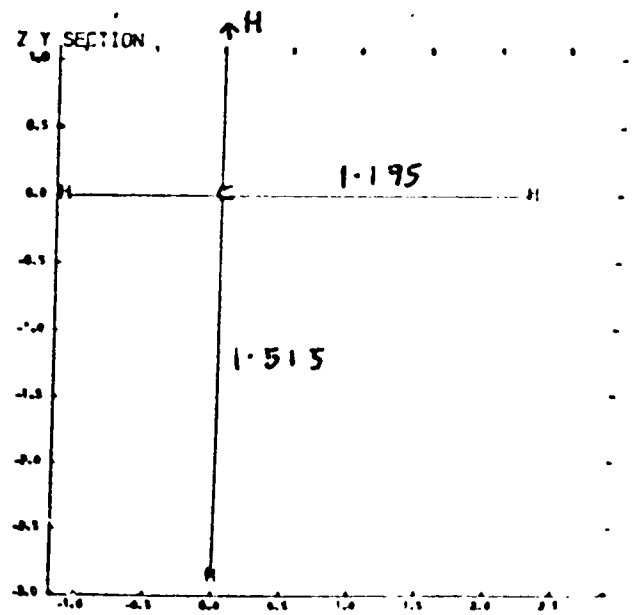




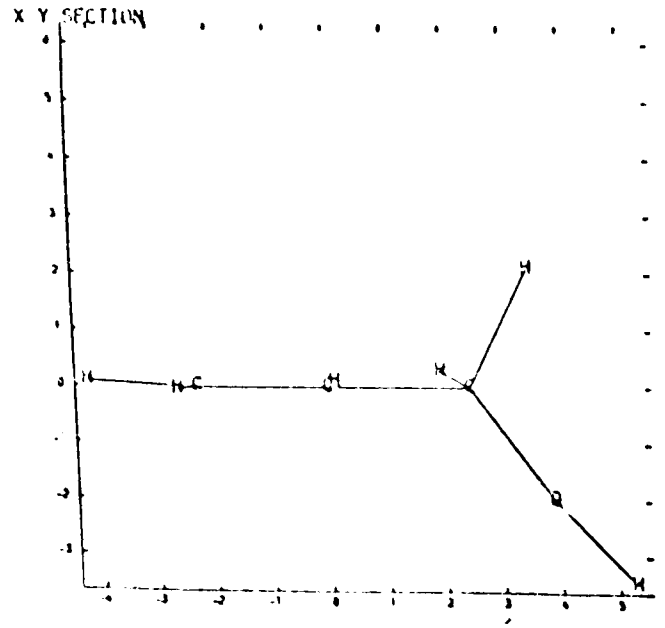
4. $CH_5^{\ominus}$ — D_{3h} symmetry.

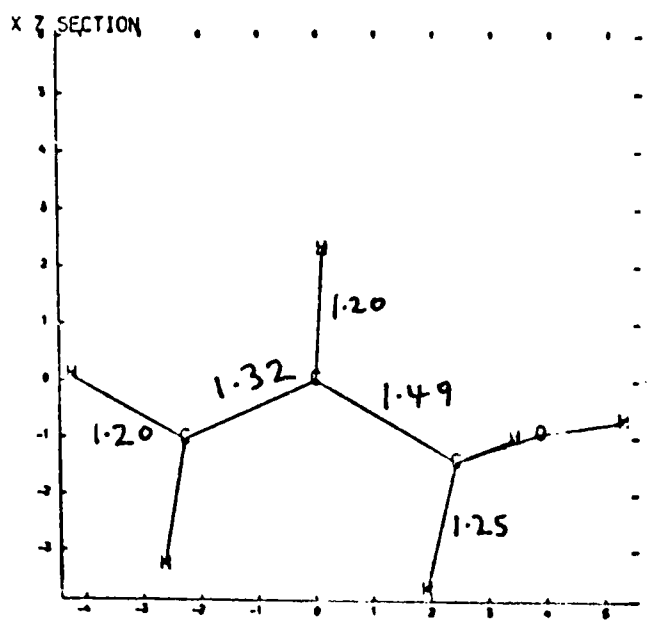


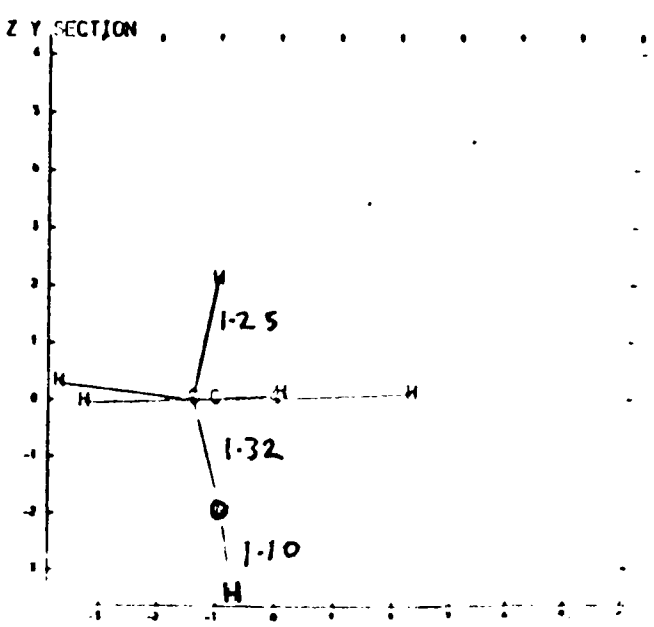




5. Allyl alcohol.





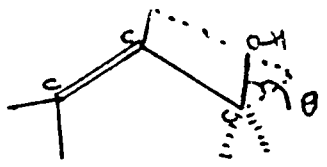


6. S_N2' – ab initio (GAUSSIAN 70) results.

ALL PARAMETERS VARIED INDEPENDENTLY, EXCEPT WHERE OTHERWISE STATED

(a) Reactants.

Allyl alcohol



Optimised parameters.

C=C	1.31 Å
C—O	1.44 Å
O—H	0.99 Å
All C-H's (together)	1.09 Å

Assumed parameters.

C—C	1.49 Å
θ	60° (Most stable of several angles investigated)
$\widehat{COH}$	104.5°

All other angles 120° or 109.5° as appropriate.

FINAL ENERGY = −189.48138 a.u.

$OH^{\ominus}$

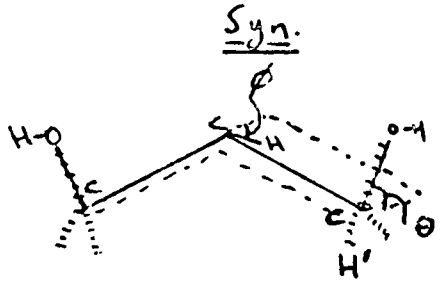
O—H 1.053 Å (optimised)

FINAL ENERGY

= −74.06487 a.u.

(b) Intermediates.

Syn.



Optimised parameters.

C⋯⋯C	1.47 Å
C⋯O	1.53 Å
ϕ	36.7°
All C-H's (together)	1.09 Å
O—H	1.01 Å

Assumed parameter.

θ	75° (Most stable of several angles investigated)
$\widehat{CCO}$	105°
$\widehat{COH}$	104.5°
$\widehat{CCH'}$ (4)	113°

FINAL ENERGY = −263.63979 a.u.

(IF ϕ=0, Energy = −263.63462 a.u.)

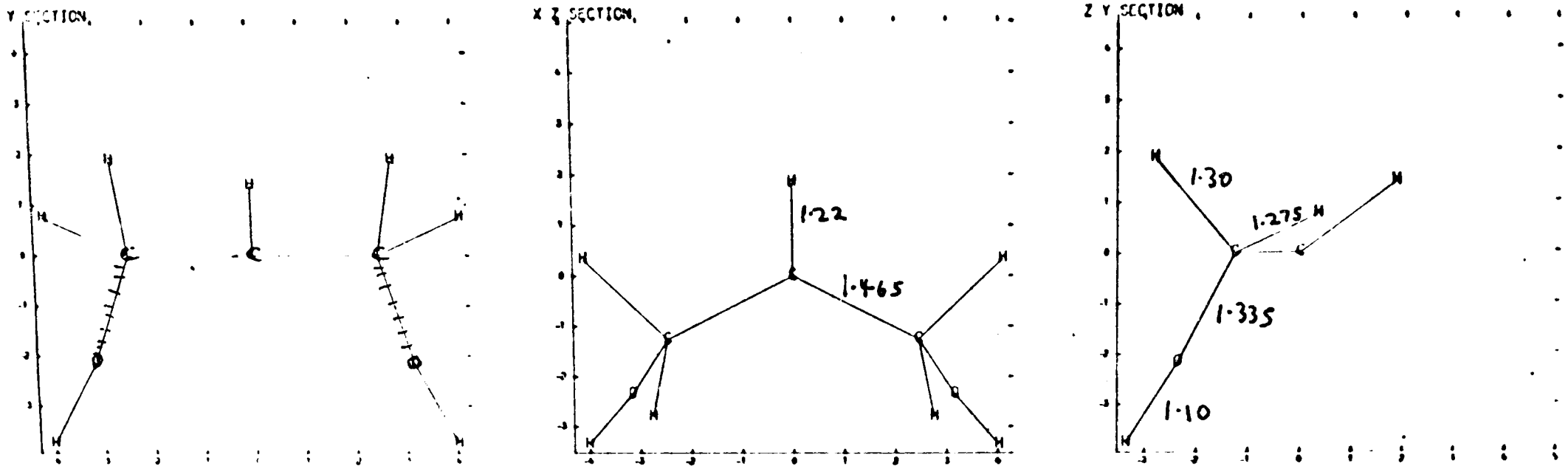
Anti.

All parameters (assumed and optimised), virtually as for Syn except $\phi = 0°$.

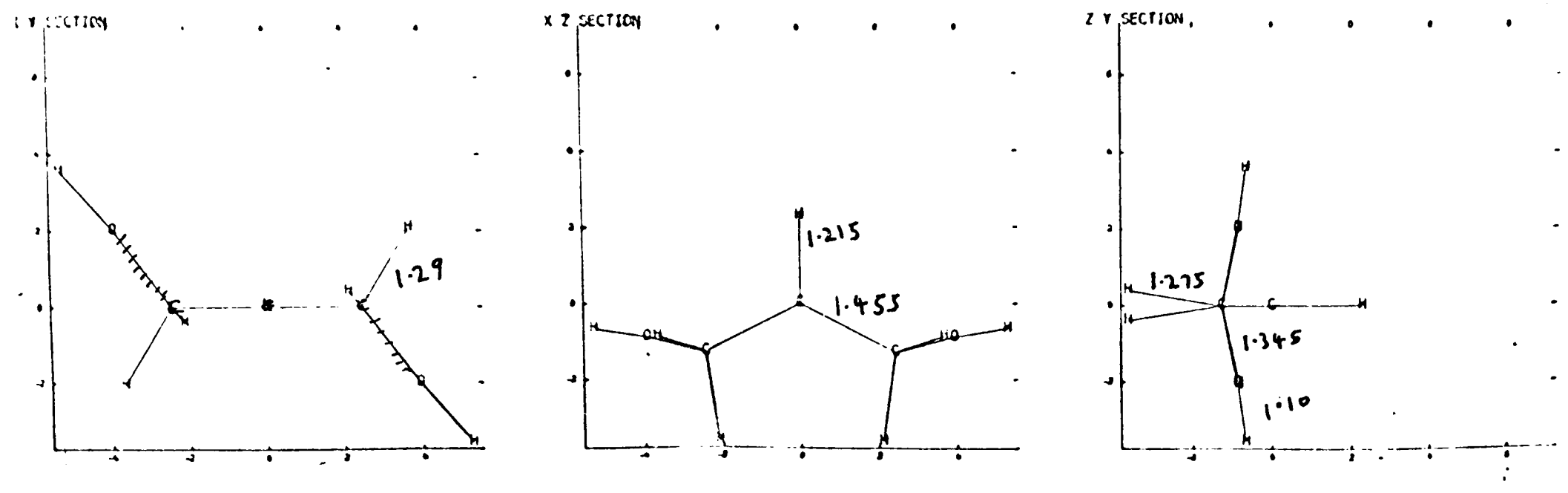
FINAL ENERGY

= 263.63804 a.u.

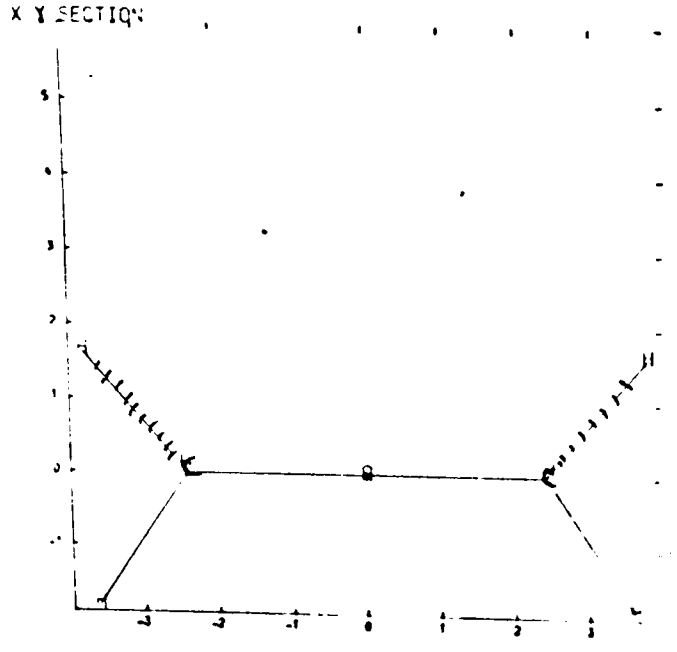
7. SN2' – syn intermediate.

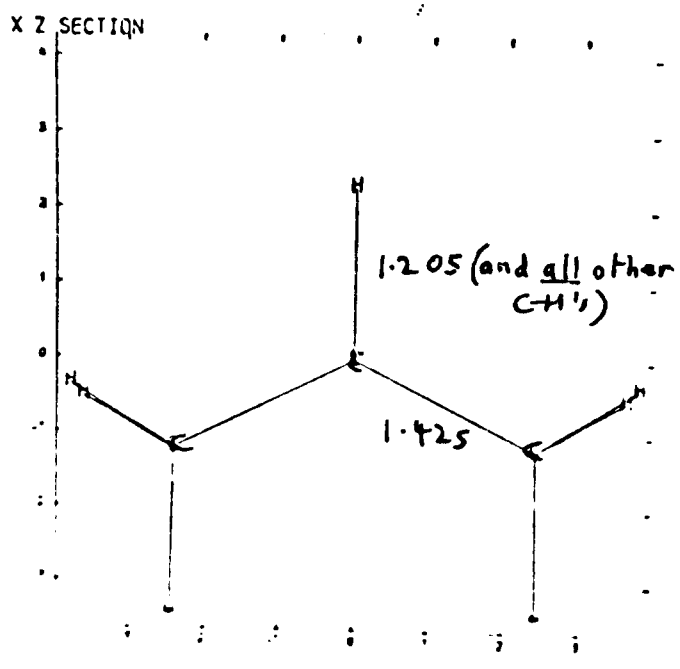


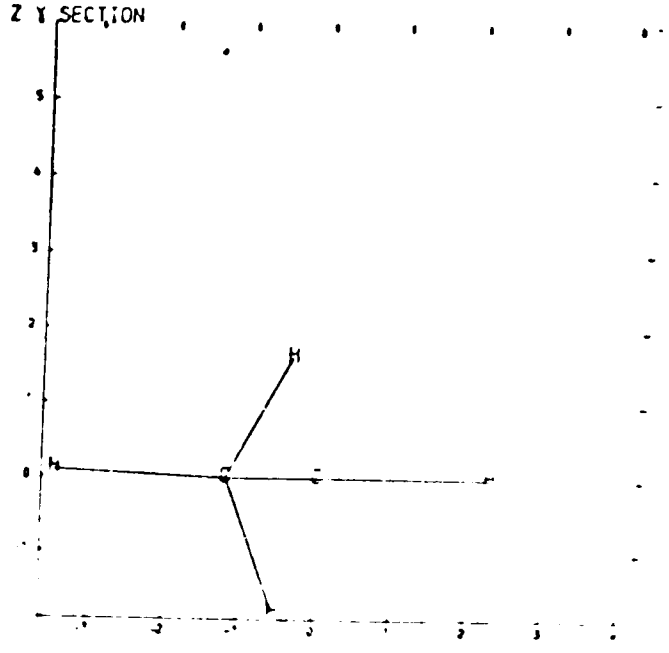
8. SN2' – anti intermediate.



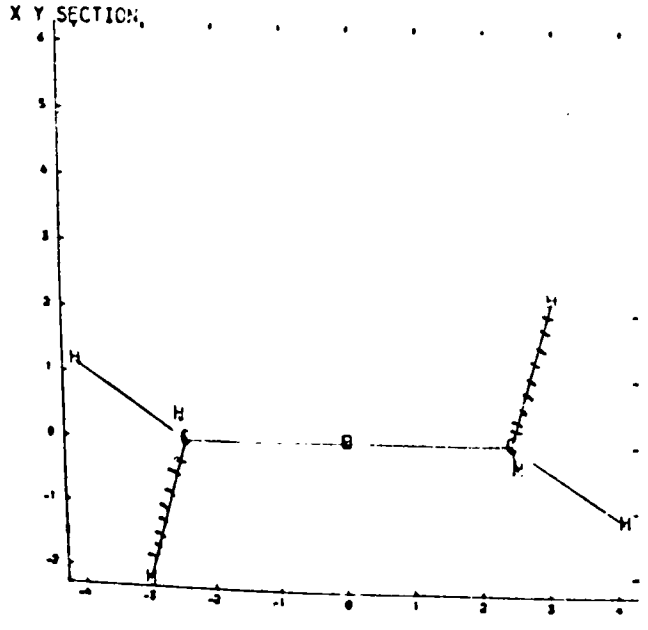
9. S_E2' – syn intermediate

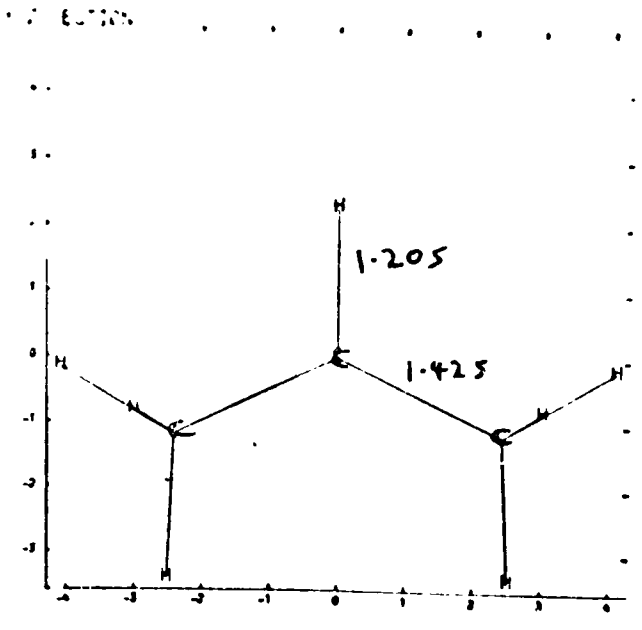


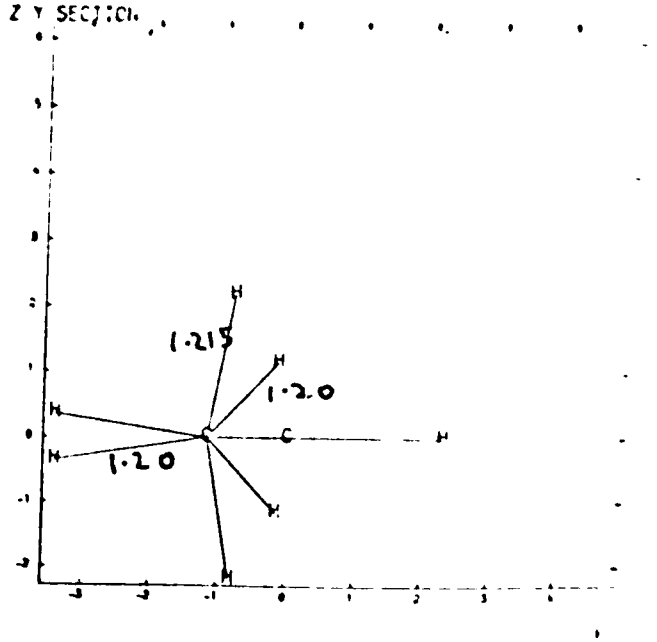




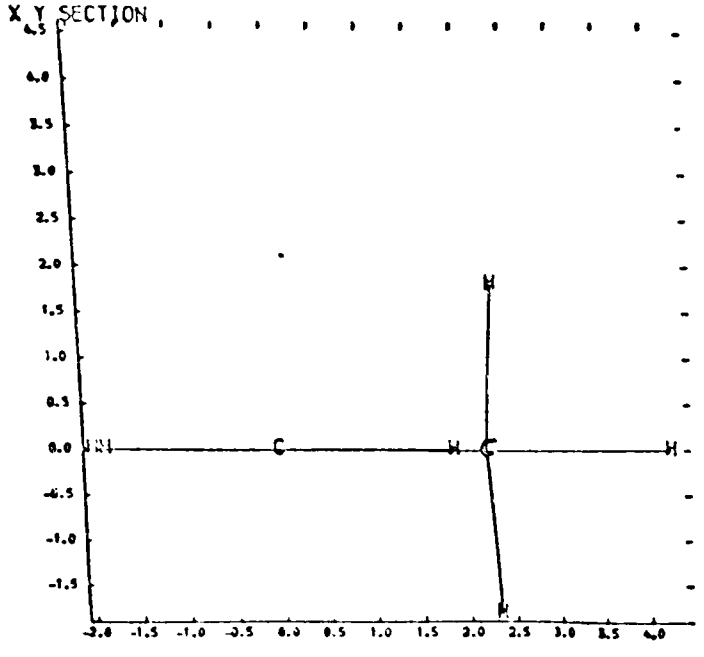
10. $SE2'$ – anti intermediate

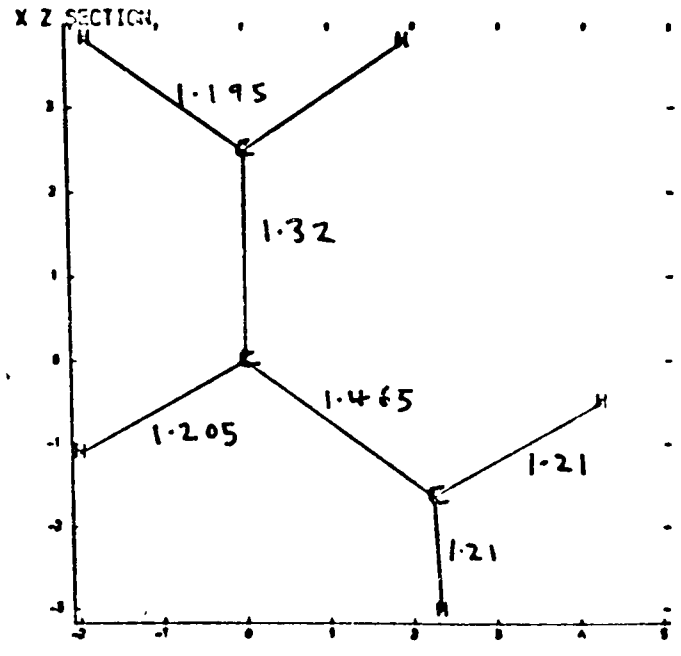


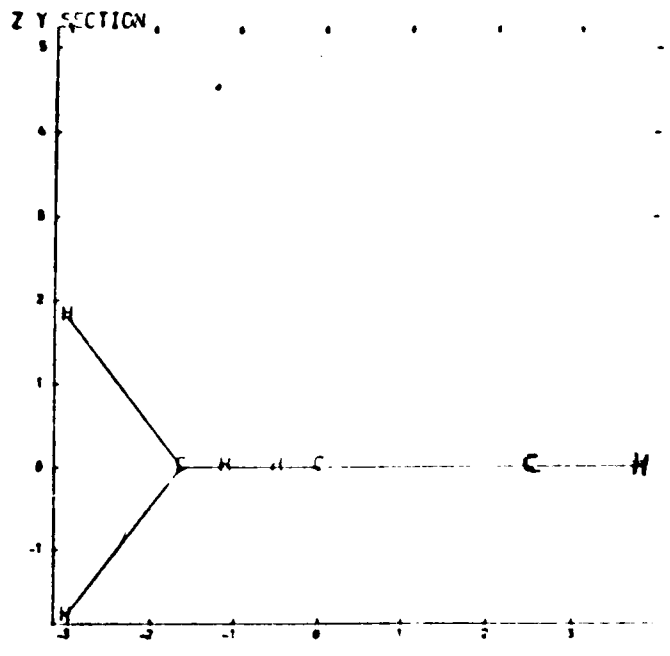




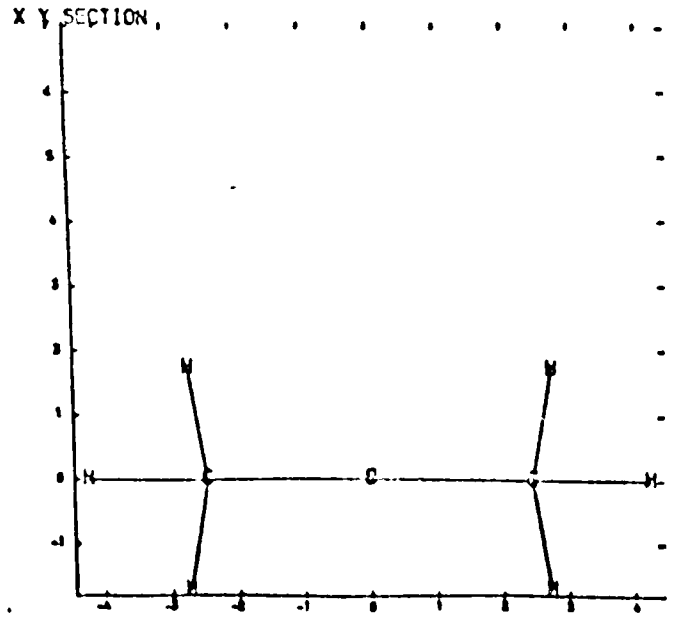
11. Propene.

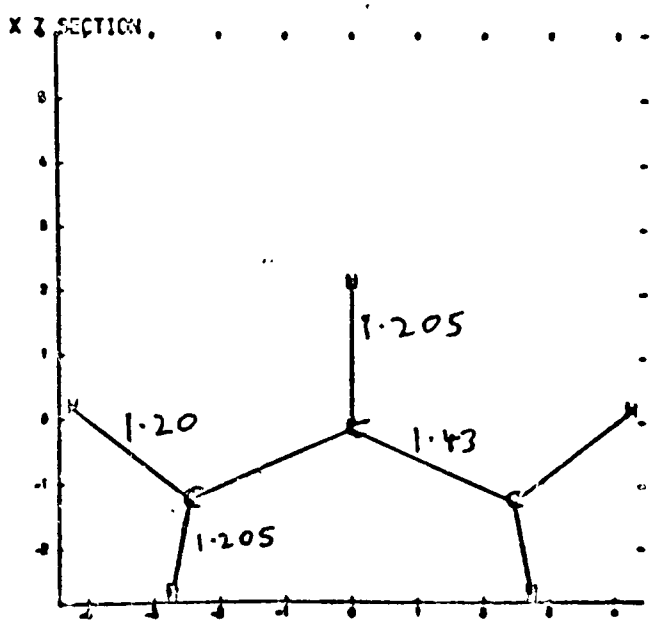


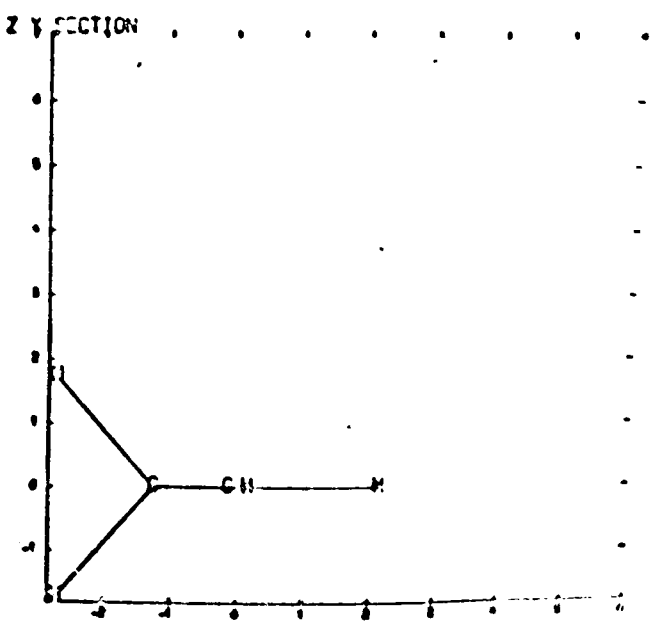




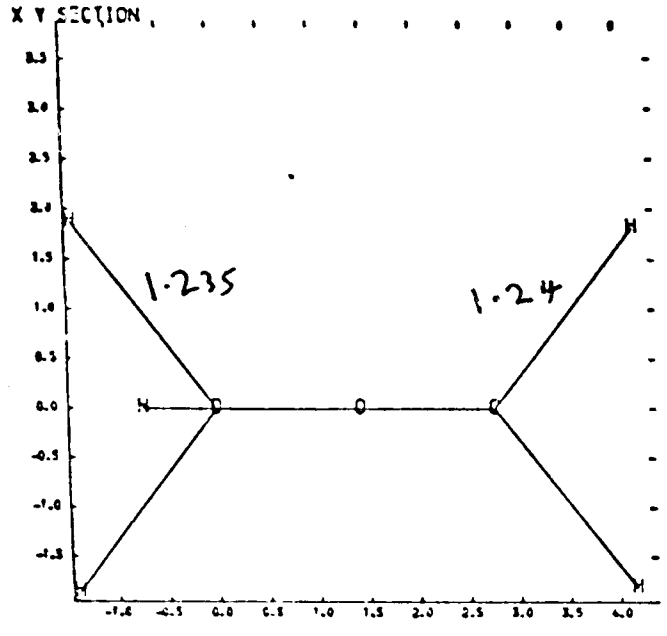
12. $C_3H_7^{\oplus}$ – eclipsed 2-propyl cation.

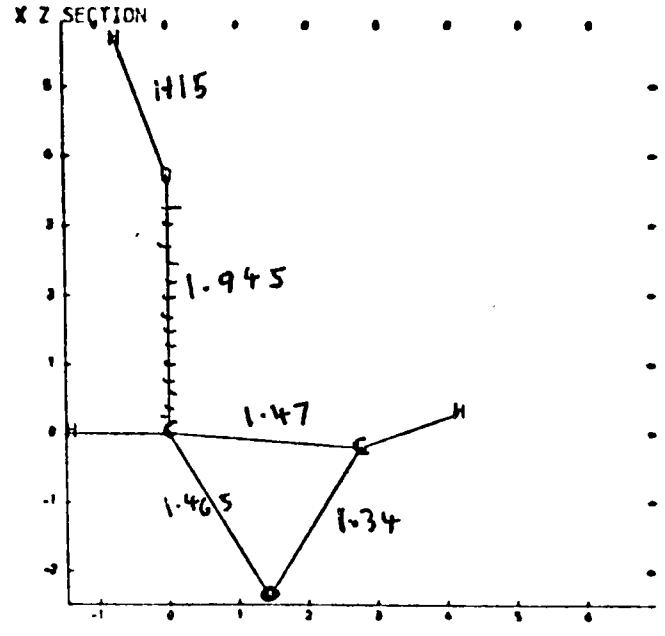


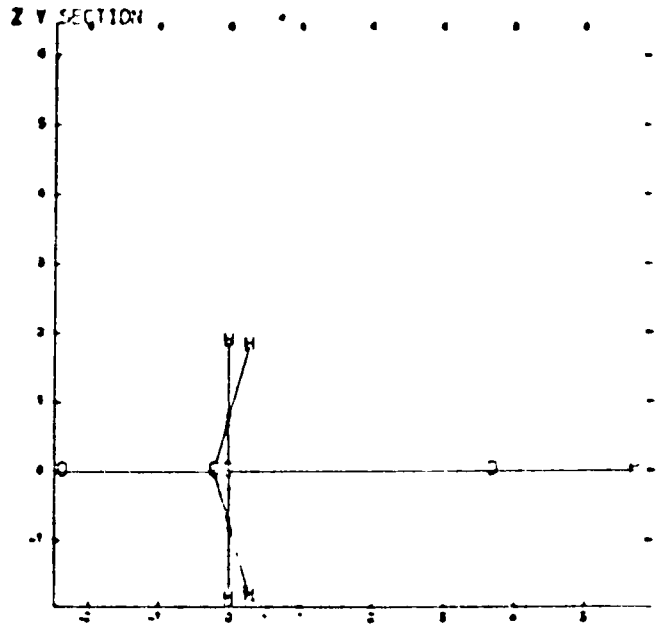




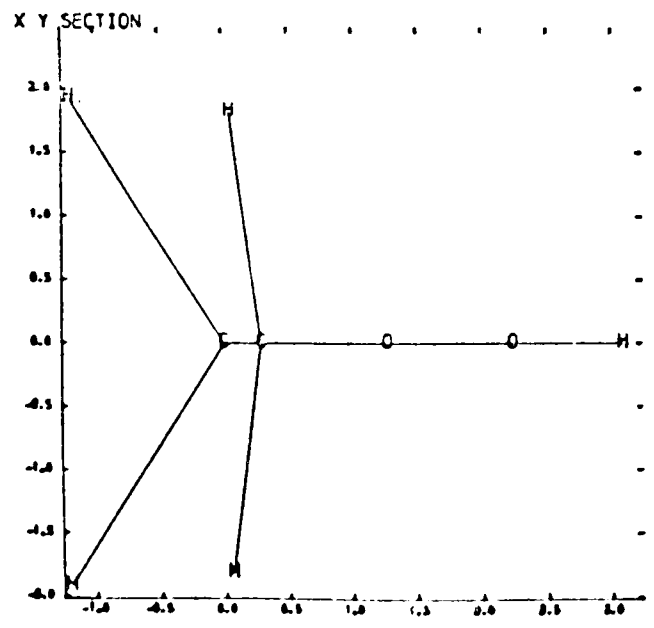
13. Ethylene oxide + $OH^{\ominus}$ – 'rear' T.S..

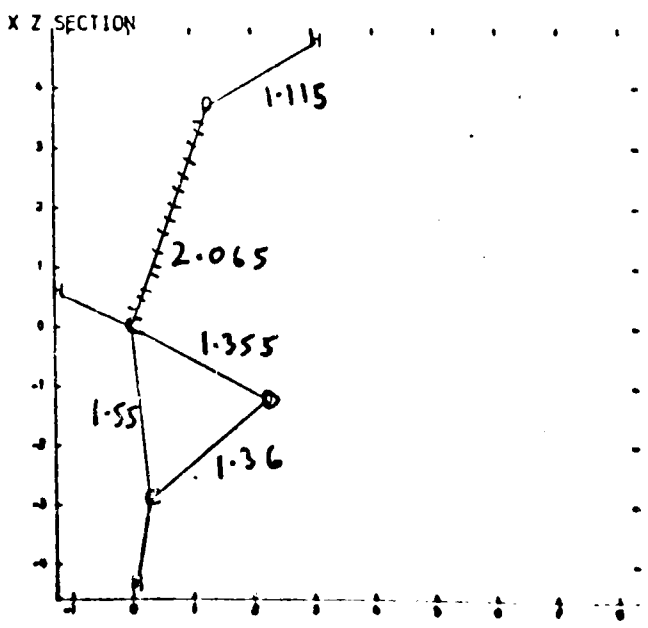


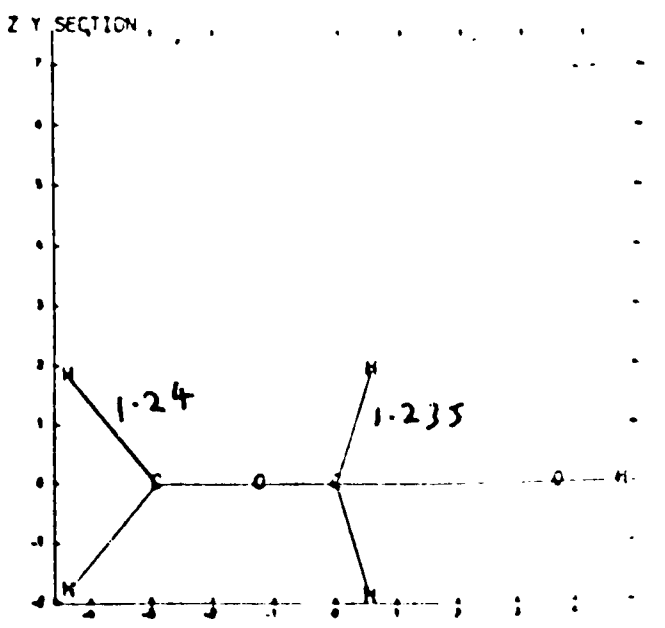




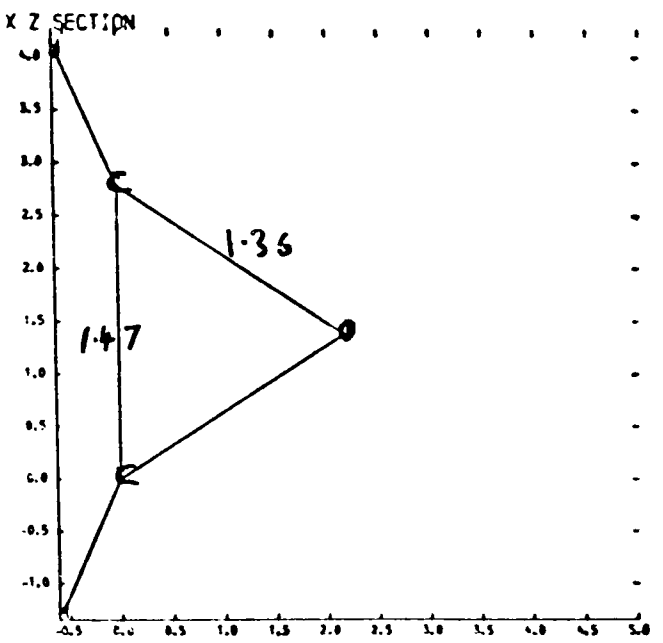
14. Ethylene oxide + $OH^{\ominus}$ – 'Front' T.S..

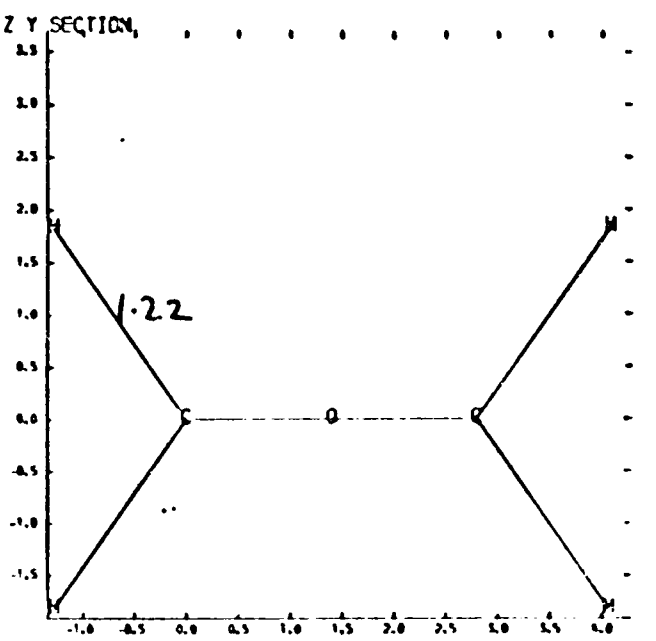


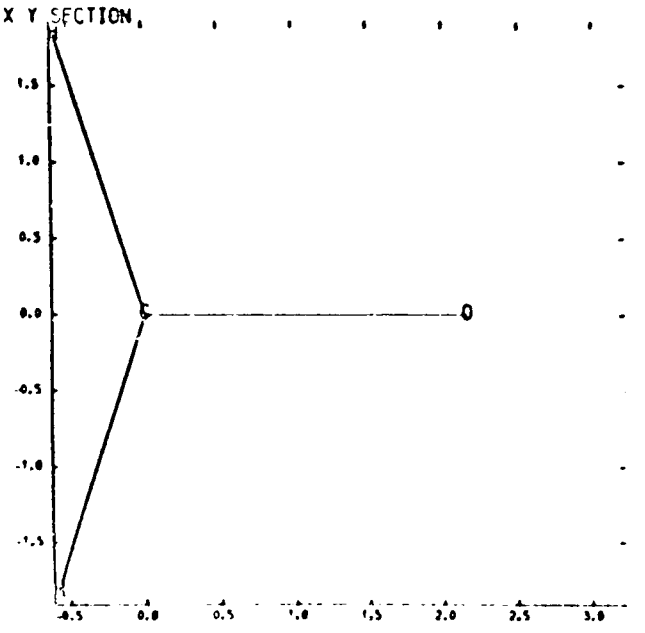




15. Ethylene Oxide.







Appendix 3.

Perturbation Theory

(a) Expansion of Molecular Orbitals.

For an old m.o. in the unperturbed system,

$$\phi_{jo} = \sum_r C_{jor} \cdot Xr$$

and the normalisation condition is $\sum_r C_{jor}^2 = 1$, because $S_{rs} = 0$, if $r \neq s$,

& $S_{rs} = 1$, if $r = s$, in the NDO approximation.

Thus the old m.o.s in the new positions will still be normalised, since the coefficients are unchanged (before mixing), even though the a.o.s have moved.

Now on mixing we have a new m.o. ϕ_i,

$\phi_i = \sum_r C_{ir} \cdot Xr$, where the Xr's are the same as in the old m.o.s, but in the new positions.

For similar reasons to above, the old orthonormal m.o.s, ϕ_{jo}, are still orthonormal in the new positions, as in the MINDO framework, this again only depends on the coefficients, which are unchanged.

$$\text{i.e. } \int \phi_{jo}^{*} \cdot \phi_{Ko} \cdot d\tau = 0, \text{ if } j \neq K$$
$$= 1, \text{ if } j = K \quad \text{in new positions.}$$

Thus expanding a new m.o., ϕ_i, in terms of the old m.o.s in the new positions.

$$\phi_i = \sum_{Ko} C_{iKo} \cdot \phi_{Ko}.$$

Multiplying by ϕ_{jo} and integrating,

$$\int \phi_i \cdot \phi_{jo} \, d\tau = C_{ijo}, \text{ (all other terms = 0)}$$

But $\int \phi_i \cdot \phi_{jo} \cdot d\tau = \sum_r C_{ir} C_{jor}$ (Because of S_{rs} approximation)

$$\therefore \quad C_{ijo} = \sum_r C_{ir} \cdot C_{jor}$$

(b) Perturbation by Geometrical Distortion.

For the unperturbed system,

$$H^o . \phi_{io} = e_i^o \cdot \phi_{io}$$

On distorting the geometry slightly, the unit overlap matrix between the ϕ_{io}'s, becomes $\underset{\sim}{S}$, where $\underset{\sim}{S} = \mathbb{1} + \underset{\sim}{S'}$. This leads to a new Hamiltonian $\underline{H}$ $(= \underset{\sim}{H^o} + \underset{\sim}{H'})$.

Thus for the perturbed system, in general,

$$H.\phi_i = e_i.S. \ \phi_i$$

However for MINDO m.o.s, the normalisation conditions are

(1) $\sum_r^i C_r^2 = 1$, as $C_r \, C_s . S_{rs} = 0$, if $r \neq s$.

(2) $\sum_r C_r^i \ C_r^j = 0$, as $C_r^i C_s^j \ . \ S_{rs} = 0$, if $r \neq s$.

As the old m.o.s in the new positions have the same coefficients, it follows that they are still orthonormal, i.e. $\underset{\sim}{S}$ is still $\mathbb{1}$. The equations for the perturbed system, in this case, reduce to

$$H.\phi_i = e_i.\phi_i$$

For which the standard results apply.